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THE CRYSTAL FORMS OF DIAMOND AND THEIR SIGNIFICANCE

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1. Introductory Statement

The crystallography of diamond presents problems of peculiar interest and difficulty. The material as found is usually in the form of complete crystals bounded on all sides by their natural faces, but strangely enough, these faces generally exhibit a marked curvature. The diamonds found in the State of Panna in Central India, for example, are invariably of this kind. Other diamonds—as for example a group of specimens recently acquired for our studies from Hyderabad (Deccan)—show both plane and curved faces in combination. Even those diamonds which at first sight seem to resemble the standard forms of geometric crystallography, such as the rhombic dodecahedron or the octahedron, are found on scrutiny to exhibit features which preclude such an identification. This is the case, for example, with the South African diamonds presented to us for the purpose of these studies by the De Beers Mining Corporation of Kimberley. From these facts it is evident that the crystallography of diamond stands in a class by itself apart from that of other substances and needs to be approached from a distinctive standpoint. It is essential, at the very outset, to emphasise the point—seemingly obvious but often overlooked—that a crystal which exhibits curved faces cannot properly be described in the usual terminology which is based on the existence of plane faces obeying the crystallographic law of rational indices.

One of the most firmly established results of physics is the dependence of the physical properties of a crystalline solid on the symmetry of its structure of which the external form is an indication. There can be little

doubt, therefore, that a study of the crystal forms of diamond, pursued from an appropriate standpoint, would prove most helpful in understanding and interpreting the many remarkable properties of this substance. These considerations and the availability of the material referred to above—some 72 specimens in all—encouraged us to undertake a critical examination of the subject. The investigation had for its object the discovery of the factors determining the general shape and other distinctive features of the crystal forms, and of the connection between them and the internal architecture of the crystal. The studies have enabled us to establish some definite propositions concerning these matters which are stated below. The evidence on which our conclusions are based will be set out fully in the course of the paper.

I. Both the internal architecture of diamond and its external form are determined by the quadrivalence of the carbon atom and its intrinsic tetrahedral symmetry in the crystal.

II. The sharply defined edges appearing on the curved surface of the crystal are its intersections with the six symmetry planes of the fundamental tetrahedron, each containing two of the valence directions.

III. The general shape of a diamond crystal stands in the closest relation with the configuration of the edges on its surface.

IV. An edge is most pronounced when it coincides exactly with a valence direction and becomes less conspicuous as it deviates from the same.

V. The vertices of the crystal are the points where four or six edges meet.

VI. The crystal symmetry of diamond as revealed by the edges on its surface is in the majority of cases that of the tetrahedral class only.

VII. While many diamonds exhibit the features characteristic of tetrahedral symmetry, there is a manifest tendency towards the assumption of forms which are common to the tetrahedral and octahedral symmetry classes.

VIII. The crystal forms of diamond exhibit a recognizable sequence on which it is possible to base a theory of their formation.

2. General Descriptive Characters

The Panna Diamonds:—Forty-three of our specimens are from the State of Panna in Central India. They are of widely differing shape, size and quality and may be considered as fairly representative of the diamonds mined in that area. As stated in the Introduction, the Panna diamonds invariably exhibit curved faces. During the senior author's two visits to the Panna State Treasury, he had the opportunity of examining several hundreds of

these diamonds, including several very large and exceptionally fine specimens and never once came across a crystal showing plane faces either alone or in combination with the usual curved forms. It is very remarkable also that though the Panna diamonds are found in conglomerate beds of obviously sedimentary origin, it is exceptional to find a specimen exhibiting signs of having undergone any wear and tear during the transit from the original site of formation to its final resting place in those beds. Indeed, amongst our 43 specimens, there are only two which give any indication of having suffered in this manner. Most of our specimens, in fact, exhibit a remarkable transparency and smooth lustrous faces on which the details are seen beautifully clear and sharp. There cannot therefore be any doubt that the Panna diamonds exhibit precisely the same form as that in which they originally crystallised.

In an earlier symposium, a paper appeared by one of us (Ramaseshan, 1944) describing and depicting the forms of the Panna diamonds. At that time, our Panna collection was not so extensive as it is now, having since been enriched by the addition of fourteen specimens of great interest from the scientific point of view. Further, at that time, we did not recognise as fully as we do now, the futility of describing curved crystal forms in the usual language of geometric crystallography. At that time also we had not discovered the physical significance of the details seen on the surface of these diamonds. The shortcomings arising from these circumstances, however, do not affect the scientific value of the diagrams, photographs and descriptive detail set out in the earlier paper. It was, in fact, the attempt to explain the facts described in that paper which led us to the present investigation.

We may here briefly recapitulate the main facts which emerged from the earlier studies. The curved surface of a Panna diamond is not a single continuous sheet, but consists of distinct sections meeting sharply along well-defined edges. These edges appear elevated above the general level of the surface to an extent depending on the angle between the sections on either side of them. This angle and the prominence of the edge vary enormously. An edge may at one part of the surface be so pronounced as to form a visible ridge, while elsewhere it may be so little conspicuous as to be seen only on careful examination under suitable illumination. The points on the surface where four or six prominent edges meet appear as protuberances or vertices of the crystal form. On the other hand, regions where the edges are inconspicuous are areas of relatively small curvature of the surface, even at points where they intersect. In a general way and subject to certain variations determined by the general shape of the diamond, the pattern of edges may be described by the statement that it divides the superficies of the crystal into

24 triangular sectors. These sectors are approximately similar to each other if the diamond is of fairly symmetric shape, while on the other hand, the sectors may differ greatly in size and shape if the diamond is of unsymmetrical form.

The Hyderabad Diamonds:—Eleven of the diamonds having their natural form as crystals included in our collection are a recent addition. They were picked out and purchased from the stock of unset stones in the possession of a firm of jewellers at Hyderabad (Deccan). No information was available regarding the origin of these stones beyond the statement that they had been detached for sale from some ancient jewellery. Since the city of Hyderabad is the nearest market to various places in the Deccan where diamonds are found, it is not improbable that the stones are of South Indian origin. All the eleven specimens are small, but they are of particular interest, being, with one exception, quite different from the Panna diamonds in their general features. They represent a combination of plane and curved forms, but the proportion of plane to curved surface varies in the different specimens. Taken together, the ten stones illustrate the successive stages of the transition from the curved faces and edges of the Panna diamonds to the form having eight plane faces separated by grooves which is the nearest approach made by diamond to the standard forms of geometric crystallography.

The South African Diamonds.—The sixteen specimens presented to us by De Beers of Kimberley for the purpose of this investigation have proved very useful in enabling us to compare the South African forms with the Indian ones and determine the relationships between them. Two items of particular interest in the collection may be mentioned here. One is a remarkably perfect example of the form of diamond first described by Haidinger, illustrations of which are to be found in the standard texts on mineralogy. The other is a triangular twin of flat tabular form with beautifully sculptured edges, presenting an interesting comparison with the rounded contours of the triangular twins found at Panna. We shall have occasion to refer to both of these specimens later in the course of the paper.

3. Some Theoretical Considerations

Geometric crystallography is based on the fact that crystals exhibit plane faces bounded by straight edges, and the descriptions given of them specify the directions of the face-normals with reference to the crystallographic axes. The obvious advantages of this system are that the directions of the face-normals are readily determined by goniometry, and that no changes are necessitated in the description by reason of any unequal development in different directions—a very common feature in actual crystals. When,

however, we seek to depict a crystal by means of a figure, what we actually do is to delineate its edges. It follows that a crystal can be described by specifying the directions of its edges instead of its face-normals, and that such a description should enable us to determine the symmetry class to which the crystal belongs quite as definitely as the orientation of its faces. In this connection, however, a minor complication which may arise has to be borne in mind, namely, that the unequal development of a crystal in different directions would not only alter the lengths of its edges, but may also bring into existence new edges along which faces which do not meet in a perfectly developed crystal intersect each other.

When the faces of a crystal are curved, as in diamond, it becomes impossible to specify the directions of the face-normals by a finite set of numbers. But it remains possible to depict the form of the crystal exactly by delineating its edges. The edges would then naturally be curved, but it may very properly be assumed that if a crystal does exhibit a set of well-defined edges on its surface, the configuration of these edges must be related in some specifiable manner to its internal structure, and hence that a study of the same would enable us to determine the symmetry class of the crystal in an unequivocal manner.

X-ray studies have made it clear that the structure of diamond is essentially based on the quadrivalence of the carbon atom. The four axes of trigonal symmetry of the crystal are, in fact, also the directions of the valence bonds which link each atom of carbon in the structure with its four nearest neighbours. It stands to reason therefore that the visible signs of crystallinity exhibited by diamond in its natural forms should also be related in some simple manner to these valence directions. A specific indication as to the nature of such relationship is obtained by considering the form of the regular rhombic dodecahedron. It is readily proved that if a diamond had this form, every one of its 24 edges would coincide with one of the valence directions. Many actual diamonds do roughly resemble a rhombic dodecahedron, but they also exhibit features which cannot be reconciled with such a description. Nevertheless, a simple examination shows that the observable edges on such diamonds do approximately coincide with the valence directions. A more exact statement would be that the edges lie in the planes which contain the valence directions taken two at a time. This statement immediately makes intelligible the features observed on such diamonds which are irreconcilable with a description of them as rhombic dodecahedra.

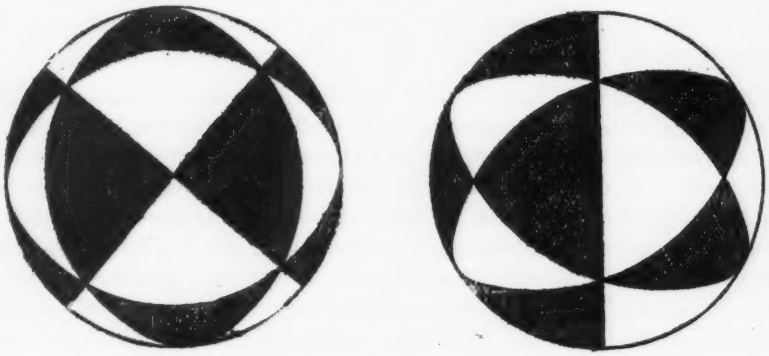
We summarise the considerations set out above in the form of two propositions.

A. The configuration of the edges on the surface of a diamond is determined by the structure of the crystal and hence should exhibit its symmetry properties.

B. The configuration of the edges is also related in a simple way to the valence directions.

4. Geometric Preliminaries

Before we proceed to discuss the observed forms of diamond in the light of the two foregoing propositions, it is useful to recall the symmetry properties of the crystal classes belonging to the cubic system. All five classes in that system have as a common feature the four axes of trigonal symmetry which are the cube body-diagonals. Taking these axes in pairs and drawing planes through them, we obtain the six diagonal planes of the cube. If these are symmetry planes, the crystal would belong to the tetrahedral class. All the elements of symmetry appearing in that class are represented by drawing through the centre of a sphere the six diagonal planes. The sphere then appears divided up into 24 equal spherical triangles.

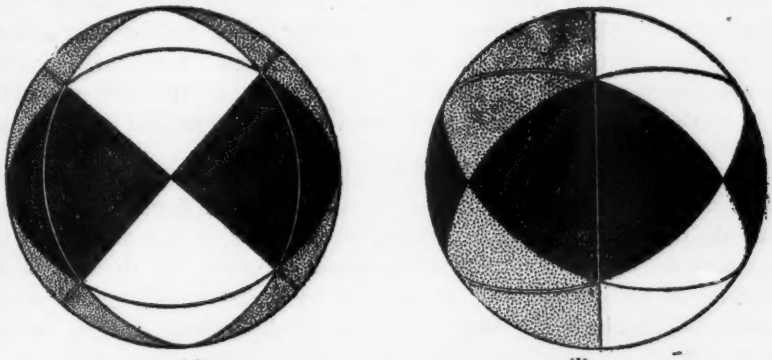


(*a*) (*b*)

Figs. 1 (*a*) and (*b*). Division of a spherical surface by the tetrahedral symmetry planes

Figs. 1 (*a*) and (*b*) represent two views of a spherical surface divided up in this way. It will be seen that there are six points on the surface where four sectors meet and eight points where six sectors meet. There are respectively the intersections with the spherical surface of the three axes of diagonal symmetry and the four axes of trigonal symmetry. Any crystal of the tetrahedral class having a regular form, *viz.*, a positive or a negative tetrahedron, a cube, a rhombic dodecahedron, a tetrakis-hexahedron or a hexakis-tetrahedron may be represented by its projection on the surface of

a sphere. The edges of the crystal would appear as the sharp dividing lines between the areas on the surface of the sphere, the number of distinct areas being the same as the number of faces in the crystal, *viz.*, 4, 6, 12 or 24 as the case may be. To illustrate this, the case of the rhombic dodecahedron is represented in Figs. 2 (*a*) and (*b*). The shorter diagonals of the rhombic faces have been retained in the figures so as to enable the similarity between Figs. 1 and 2 to be perceived.



(*a*) (*b*)

FIGS. 2 (*a*) and (*b*). Rhombic dodecahedron projected on a sphere

If, besides the six diagonal planes, the three axial planes of the cube are also planes of symmetry, the crystal would belong to the octahedral class. The elements of symmetry appearing in that class may be represented by drawing all the nine planes through the centre of a sphere. The surface of the latter would then appear divided up into 48 equal spherical triangles.

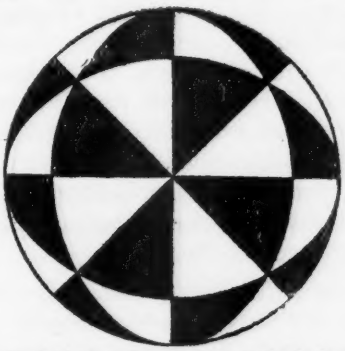


FIG. 3. Division of spherical surface by the octahedral symmetry planes

Fig. 3 illustrates the division of a spherical surface in this way by the symmetry planes of the octahedron. A regular crystal having the most

general form of this class with 48 similar faces could be represented by its spherical projection, the edges of the crystal appearing as the dividing lines between the sectors of the sphere. Particular cases of the class with a smaller number of similar faces could also be represented in the same way by the simple device of leaving out some of the dividing lines on the surface and thereby reducing the number of distinct areas into which it appears divided. For instance, a regular octahedron would be represented by Fig. 3 with the six diagonal planes of symmetry omitted and only the three axial planes of symmetry retained, the surface of the sphere would then appear divided into 8 equal areas separated by sharp dividing lines. It would, of course, be impossible to exhibit the form of an octahedral crystal with the aid of Fig. 1, since the three axial planes of symmetry are not present in that figure.

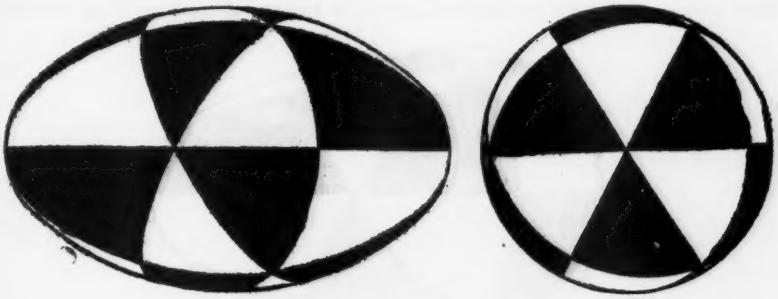
5. The Configuration of the Edges

Even from the results of the earlier studies of the forms of the Panna diamonds referred to above (Ramaseshan, *loc. cit.*), it is evident that the edges seen on the surface of these diamonds represent the division of the superficies of the crystal into 24 sections by the symmetry planes of the fundamental tetrahedron. Many of the diamonds do indeed show marked deviations from the simplicity and regularity of the pattern depicted in Fig. 1. These deviations are however readily explained and do not represent any essential departure from the principles which determine the configuration of the pattern.

In the first place, the actual shape of the diamond has to be taken into consideration. The influence of this may be illustrated by considering the intersection of the symmetry planes of a tetrahedron with various surfaces other than a sphere, *e.g.*, a prolate spheroid, an oblate spheroid or an ovaloid of revolution, which roughly represent the shape of the smaller Panna diamonds. In dealing with such cases, it is natural to suppose that the orientation of the tetrahedral axes with respect to the surface would not be arbitrary, but would be related to it in some specific fashion, *viz.*, one of the trigonal axes of symmetry would coincide with the rotation axis of the surface. It is noteworthy that this view is borne out by the actual facts, *viz.*, that the configuration of the edges on the surface of a diamond is very clearly related to the general shape of the crystal.

The division of the surface of a prolate spheroid into 24 sectors by the six diagonal planes of symmetry is shown in Fig. 4. Fig. 4 (*a*) is a side view and Fig. 4 (*b*) is an end view. The sectors of the surface are still of roughly triangular form, but they are now of unequal area, those near the ends being considerably enlarged in relation to the others. A prolate spheroid has an

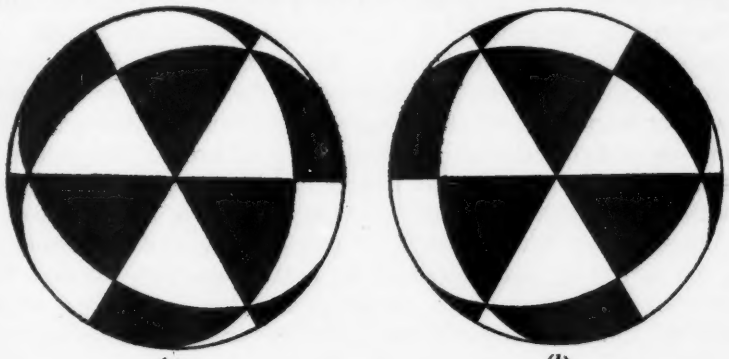
axis of rotation and a plane of symmetry bisecting that axis. But the pattern on its surface evidently does not exhibit these features.



(*a*) (*b*)

FIGS. 4 (*a*) and (*b*). Division of a prolate spheroid by the tetrahedral symmetry planes

The division of the surface of an oblate spheroid into 24 segments by the six diagonal planes of symmetry is illustrated in Figs. 5 (*a*) and (*b*), the



(*a*) (*b*)

FIGS. 5 (*a*) and (*b*). Division of an oblate spheroid by the symmetry planes of a tetrahedron

two figures being the front and back views of the surface. It will be noticed that the front and back views are different and that one of them would require to be rotated through 180° to enable them to be brought into coincidence, thereby showing clearly that while the oblate spheroid has a plane of symmetry bisecting its axis of rotation, the pattern on its surface does not share that feature. Later in the paper, we shall have occasion to consider the features appearing in Figs. 5 (*a*) and (*b*) in relation to the theory of formation of the flat triangular twins of diamond.

Fig. 6 illustrates the division of the surface of an ovaloid of revolution into 24 segments by the symmetry planes of a tetrahedron. The figure of

the ovaloid does not possess a centre of symmetry and hence a pattern drawn on its surface exhibits the tetrahedral symmetry in a more obvious fashion than similar patterns on the surface of a sphere or spheroid of revolution.

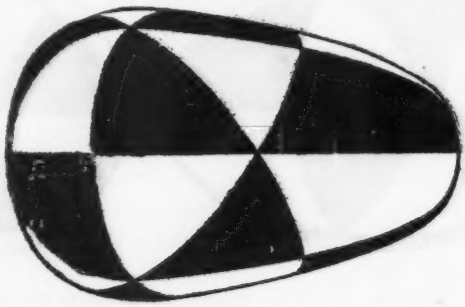


FIG. 6. Division of an ovaloid of revolution by the symmetry planes of a tetrahedron

In the models illustrated in Figs. 4, 5 and 6, the six diagonal planes of symmetry were drawn so as to pass through a single point within the surface, *viz.*, the centre of the spheroid or the centre of mass of the ovaloid. As a consequence, the patterns are similar to that drawn on the surface of a sphere in their general features, *viz.*, the division of the surface into 24 segments of triangular shape, four of which meet at six common points on the dyad axes and six at eight common points on the triad axes. The patterns are thus fundamentally related to the pattern of edges presented by a hexakis-tetrahedron or a tetrakis-hexahedron with 24 exactly similar faces. We know, however, that when the general shape of a crystal departs from regularity, the pattern of edges exhibited by it is substantially altered. While the *directions* of the edges which persist remain the same, their positions are altered, and new edges appear along the lines of intersection of the planes which did not previously meet. A similar situation would arise in our present problem of the configuration of the edges on a curved surface, and similar results would naturally follow. Hence, the configuration of the edges in the vicinity of the dyad and triad axes would be altered to an extent varying with the general shape of the diamond and to different extents at the various points. The nature of such variations may be readily deduced by shifting the edges laterally while retaining their general directions and drawing intermediate edges connecting the broken ends together.

This has been done in Fig. 7 for the case of four edges which fail to meet exactly on a dyad axis, with the result that a fresh edge connecting up the broken ends appears on the surface. It may be remarked that this type of irregularity is seldom noticed in diamond. The reason for this is that in the

vicinity of the dyad axes, the valence directions lie in two perpendicular planes and the edges meeting on these axes are usually very pronounced.

FIG. 7. Pattern of edges in the vicinity of a dyad axis

On the other hand, the six edges which run towards a triad axis often fail to meet exactly on that axis when they traverse a part of the surface which is very nearly flat. The various types of deviation which may be expected to occur are indicated by the diagrams in Fig. 8. It may be remarked that they correspond closely to the features actually observed in our specimens.

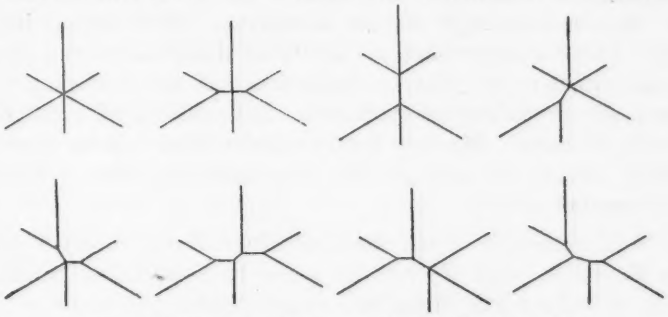


FIG. 8. Pattern of edges in the vicinity of a triad axis

All the Panna diamonds without exception exhibit on their surface a pattern of edges which may be described as its intersections with the tetrahedral planes of symmetry of the structure—subject to the modifications described and illustrated above. This fact is all the more remarkable when it is recalled that some of the specimens in our collection bear no resemblance whatever to the conventional descriptions of a crystal. The actual configuration of the edges varies with the shape of the diamond and when this is irregular, the edges meander in their course. We shall refer to the points on the surface where four and six edges meet respectively as the dyad and triad vertices of the crystal. The actual shape of any particular specimen is closely connected with the configuration of the edges in the vicinity of the dyad and triad axes and the relative prominence of the two types of vertices. There are, of course, various possibilities, and many of them are illustrated

by the specimens in our collection. We shall return to these matters later in the paper, but meanwhile we may turn to the fundamental question—What is the crystal symmetry of diamond?

6. The Crystal Symmetry of Diamond

As illustrated in Fig. 3, the planes of symmetry in the octahedral class divide the sphere into 48 equal sectors. If diamond had octahedral symmetry of structure, we may expect it to exhibit such a subdivision, or at least the edges lying in the axial planes of symmetry. There is not the slightest hint or indication of any such edges in the Panna diamonds. Geometric crystallography tells us that the tetrahedral and octahedral symmetry classes have some forms in common, *viz.*, the cube, the rhombic dodecahedron, and the tetrakis-hexahedron. If a substance crystallised exclusively in these forms, it would not be possible to decide between the two alternative possibilities. A decision can only be based on the appearance or non-appearance of forms definitely indicative of the higher or the lower symmetry as the case may be. We are accordingly justified in applying similar tests in the case of diamond. The non-appearance in the Panna diamonds of the edges lying in the axial symmetry planes is an indication that we are dealing with only the lower and not the higher symmetry. But evidence of a more positive character is desirable. We must however know what it is we have to look for. Here, again, we may usefully draw upon the ideas and results of geometric crystallography.

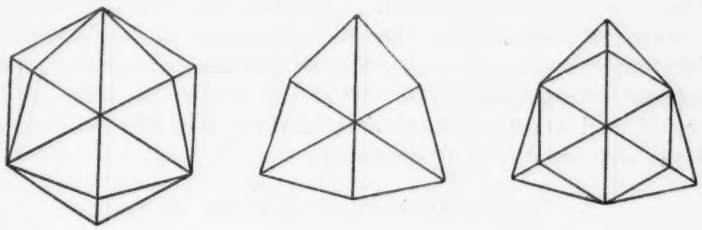
Fig. 9 (*a*) represents a tetrakis-hexahedron viewed along a dyad axis in either direction, while (*b*) and (*c*) represent a hexakis-tetrahedron also viewed along a dyad axis in the two opposite directions respectively.

(*a*) (*b*) (*c*)

Figs. 9 (*a*), (*b*) and (*c*). (*a*) Tetrakis-hexahedron; (*b*) and (*c*) Hexakis-tetrahedron viewed along a dyad axis

Fig. 10 (*a*) represents a tetrakis-hexahedron viewed along a triad axis in either direction, while Figs. 10 (*b*) and (*c*) represent a hexakis-tetrahedron viewed along a triad axis in the two opposite directions respectively. The forms illustrated in Figs. (9) and (10) both belong to the tetrahedral symmetry class, but the tetrakis-hexahedron can also be regarded as exhibit-

ing octahedral symmetry, the dyad axis then becoming a tetrad axis passing through a centre of symmetry. As can be seen from a comparison of the figures, the characteristic feature of tetrahedral symmetry is that the dyad vertices appear as ridges instead of as peaks, while the triad vertices appear as peaks and as domes respectively at the opposite ends of each axis instead of as peaks at both ends.



(*a*) (*b*) (*c*)

FIGS. 10 (*a*), (*b*) and (*c*). (*a*) Tetrakis-hexahedron ; (*b*) and (*c*) Hexakis-tetrahedron viewed along a triad axis

Examination of our Panna collection discloses in numerous cases the specific features of tetrahedral symmetry indicated above. It is a very common occurrence to find the dyad vertices appearing as elongated ridges formed by the meeting of two edges nearly parallel to each other, while the two other edges which are transverse to them go up and down the slopes of the ridge. Then, again, one frequently finds the eight triad vertices falling clearly into two groups, one set of four forming fairly well-defined peaks, while the other set of four opposite to them appear as flattened domes. It is very significant also that such configurations of the dyad and triad vertices appear in association with each other. In other words, it is the same diamonds that either show or do not show the stated features in respect of the dyad and triad vertices. Further, these features are clearly related to the general shape of the diamond. The crystals that do not exhibit these features are of highly symmetrical form. On the other hand, the specimens that do exhibit these features possess a symmetry of general shape which is obviously of a lower order. Some of the finest diamonds in our Panna collection —beautiful water-white crystals with smooth lustrous faces—present an external form which does not possess a centre of symmetry. It is impossible in the face of these facts to doubt the truth of the proposition that *the internal symmetry of the diamond structure is that of the tetrahedral class only and not that of the octahedral,* at least in all the cases now under consideration.

It remains to be explained, however, why diamond seems to prefer the forms whose symmetry may be indifferently assigned either to the lower or

the higher class, and why even in the forms in which the lower symmetry is observable, it does not appear as conspicuously as might have been expected. One possible explanation is that the more symmetric forms have a smaller surface per unit volume than the less symmetric ones. If, as the curvature of the surfaces suggests, diamond was formed by solidification from carbon liquefied under pressure, the form having the smaller surface would have less surface energy and is therefore more likely to be assumed at the instant of solidification. The second possible answer, which is supported by much relevant evidence, is that the positive and negative tetrahedral forms appear intermingled in the crystal. If this be the case, the crystal form would tend to imitate octahedral symmetry even if it does not exhibit the specific characters of that symmetry.

7. Classification of the Crystal Forms

A survey of all the specimens in our collection indicates that in spite of the great variety of forms exhibited by diamond, it is possible to arrange them in a regular sequence which is evidently connected with the physical circumstances of their formation. The ordering of the forms in such a sequence is obviously an advantage. It avoids the necessity for a minute description of all the individual specimens, and it also enables us, at least tentatively, to put forward a physical explanation of the features appearing in them. Indeed, we may advantageously reverse the order and derive from physical considerations an idea of what the forms of diamond should be and then proceed to fit the observed forms into a sequence based on such considerations.

It appears highly probable that diamond results from the solidification of carbon which has assumed the liquid state under conditions of high pressure and temperature. The state of the atoms in the liquid state is an important point needing consideration. The thermal agitation would certainly prevent a perfect ordering of the valence bonds within the liquid. Hence, it follows that the molten carbon would assume a rounded shape and this would be the more likely, the smaller the volume under consideration. Solidification is accompanied by a fixation of the valence bonds but not necessarily by any radical change of shape. On this basis, it is easy to understand why the crystals formed have curved faces. It may be remarked that the smaller diamonds in our Panna collection exhibit a highly marked curvature of the surface on which a pattern of edges appears as described earlier in the paper. The formation of these patterns is readily explained. At the surface of the molten carbon there would be some free valences which may attach themselves to the surrounding material. The valences not thus

disposed of would link each carbon atom to its three nearest neighbours on the surface and hence would tend to align them with respect to its position in the valence directions. Accordingly, the first indication of the regular internal structure manifesting itself on the surface of the solidified material would be the formation of edges along the directions of the valence bonds, or in the planes containing them which are also the tetrahedral planes of symmetry of the structure.

If the edges of the crystal could align themselves completely along the valence directions, the surfaces between them would be plane, and the form of the crystal would be that of the rhombic dodecahedron. However, the curvature of the surfaces would prevent such a complete ordering of the edges. In consequence, the form would only approximate to a rhombic dodecahedron; the edges would not stop at the triad vertices but would be continued along the shorter diagonals, thereby dividing the superficies into 24 parts and not 12. Since these " continuation edges " deviate considerably from the valence directions, they would be relatively inconspicuous and would also meander on the surface to fit its varying curvature. These features are exhibited by several of our South African specimens. One of them (N.C. 26) is a beautiful crystal which might easily be mistaken for the regular rhombic dodecahedron of geometric crystallography, but is seen on a more careful examination to exhibit the features indicated above. The other dodecahedroid diamonds are less symmetrical in shape and exhibit corresponding variations in the configuration of their edges. These variations, however, are fully explicable on the same basis as in the case of the Panna diamonds already discussed in the foregoing pages.

If the valence bonds within the liquefied carbon have at least a semblance of the regular ordering which exists in the crystal, it would follow that the form assumed by the mass would deviate notably from a spherical shape. In a separate paper by Ramaseshan appearing in the present symposium, it is shown that the surface energy per unit area varies with the orientation of the surface in respect of the valence directions, being a minimum in the directions normal to the triad axes and a maximum in directions normal to the dyad axes. Accordingly, the liquid mass would tend to assume the shape of an octahedron with rounded edges, the largest proportion of the area appearing in the vicinity of the triad axes and the smallest near the dyad axes. On solidification, this general shape would be maintained but modified by the formation of the usual pattern of edges in the planes containing the valence bonds. Many of the larger Panna diamonds, including three examples in our collection (N.C. 2, N.C. 4, N.C. 8), have the shape indicated here. They may be referred to as " octahedroid " diamonds, but

are not true octahedra, since they do not exhibit any edges in the axial planes. It may be remarked that the edges in the vicinity of the triad axes are much less conspicuous in the octahedroid diamonds than in the dodecahedroids, since they necessarily deviate more from the valence directions.

A further stage in the sequence of the crystal forms of diamond is reached when the influence of the thermal agitation is diminished sufficiently to enable the surface of the molten carbon to adjust itself exactly to the condition of minimum surface energy. This would exhibit itself by the surface in the immediate vicinity of the triad axes appearing as perfect planes in the solid crystal. The subsequent stages in the sequence would correspond to increasing areas of such plane areas in the crystal and a corresponding contraction of the curved surfaces, until finally a crystal form is attained in which nearly the whole surface consists of optical planes normal to the triad axes of symmetry.

The appearance of optically plane or "splendent" faces in combination with curved surfaces is represented in all its stages in our collection. The first indication of it to appear is a peculiar waviness or rippling of the surface in the vicinity of the triad vertices, often of a regular character and forming a hexagonal network of lines surrounding these vertices. The next stage in the sequence is the appearance of plane areas at and around these vertices. If these are continuous and of sufficient extent, they appear as a truncation or slicing off of the curved surface of the crystal and indeed have the form which would result from such a process, *viz.*, a hexagon with three acute and three obtuse angles, the vertices appearing exactly at the points where the edges running across the curved surfaces meet the plane. Not infrequently also, the planes appear at the top of a succession of terraces. These terraces run parallel to the perimeter of the plane area, and the edges which have traversed the curved surfaces can be traced through the whole series of terraces up to the plane surface before they finally disappear. As the plane areas enlarge further in extent and the curved surfaces diminish correspondingly, the terraces or slopes—sometimes both terraces and slopes —fringing the plane areas persist, with the result that the crystal presents finally the appearance of an octahedron with deep grooves along its edges. The successive stages by which this result is reached can be followed in the Hyderabad specimens in our collection, thereby making it evident that it is not an accidental circumstance but a specific feature of the crystal forms of diamond.

8. The Haidinger Diamond

As mentioned earlier, our South African collection includes a magnificent example (N.C. 25) of the particular form of diamond originally

observed and figured by Haidinger and of which illustrations are to be found in the standard treatises on mineralogy. The general form is that of an octahedron, but the octahedral edges are absent. In their place, we have the special feature of the form, namely, conspicuous V-shaped grooves with smooth surfaces which widen from the middle outwards. Four of these grooves meet at each vertex of the octahedron and terminate in four sharp straight edges converging to a point on the symmetry axis. ***These edges lie in the planes containing the valence bonds, and our measurements indicate that they are parallel to the valence directions.*** They form part of the system of edges lying in the valence planes characteristic of all diamonds. Continuations of them, though much less conspicuous, may be traced running up the terraces on the faces of the octahedron and disappearing at the vertices with acute angles on each face. Another set of edges can be seen cutting across each groove and dividing it at its narrowest part into two parts sharply inclined to each other. These same edges can also be traced climbing the terraces and meeting the plane octahedral faces at the vertices with obtuse angles.

Apart from the fact that the particular specimen is a remarkably perfect one, the features which it exhibits can also be seen in several of our Hyderabad diamonds. It is therefore clear that the Haidinger diamond is not a rare or accidental occurrence but is a typical form of deep significance in the crystallography of this substance. The appearance of grooves or re-entrant edges is a characteristic feature of twinning, and in view of the independent evidence showing that the crystal symmetry of diamond is ordinarily that of the tetrahedral class, the only reasonable description of the Haidinger form is that it is an interpenetration twin of positive and negative hexakis-tetrahedra truncated by planes normal to the trigonal axes. Further, since the form mimics octahedral symmetry, it furnishes an excellent example of the result of such interpenetration in suppressing the external manifestation of the inherent tetrahedral symmetry of diamond.

9. The Triangular Twins

The ideas developed in the preceding pages enable us to offer a simple explanation of the formation and peculiar shape of the well-known "macles" or twin diamonds of triangular form and of small thickness, examples of which are often forthcoming. Referring again to Figs. 5 (*a*) and (*b*) on an earlier page in which the front and back views of an oblate spheroidal model were represented, the remark may be recalled that for these two views to become identical, it would be necessary to rotate one through 180° with respect to the other. In the figures, the pattern of edges is represented as

lying on the surface of the model. Actually, however, the dyad vertices would appear elevated above the surface, while the triad vertices would tend to be suppressed and become relatively inconspicuous, as is indeed the case in the majority of diamonds for reasons already explained. Hence, an oblate spheroidal diamond would tend to assume a triangular shape having its vertices on the dyad axes of the pattern, but the triangles on the two faces would be set oppositely, *viz.*, vertex to base and base to vertex. Indeed, some of the specimens in our Panna collection (N.C. 6, N.C. 12) show such a form. The thinner the diamond, however, the greater would be the probability that this incompatibility between the front and the back of the same crystal would be redressed during its formation by one half of the form swinging round through 180° with respect to the other, thereby resulting in the formation of a triangular twin in which the two halves fit each other perfectly, vertex to vertex and base to base.

The pattern of edges formed by the intersections of the tetrahedral symmetry planes with the two surfaces of a model twin of triangular form is represented in Fig. 11. Only one side of the model is shown, since the other would be identical in the twin. Examination of the triangular twins in our Panna collection (N.C. 9 and N.C. 23) reveals a pattern of edges on their faces and their edges which corresponds closely with that represented in Fig. 11.

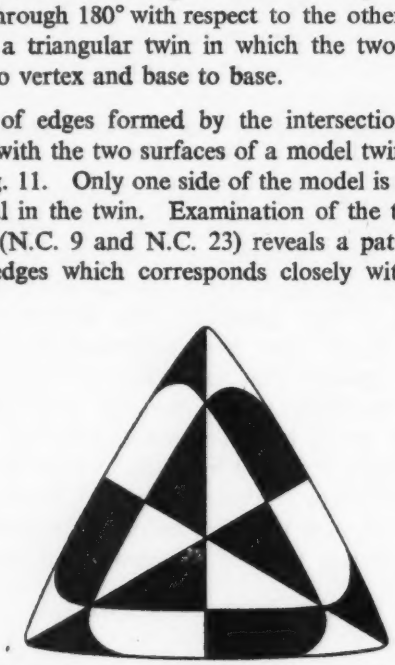


FIG. 11. Intersection of the tetrahedral symmetry planes with the surfaces of a triangular twin

One of the South African specimens in our collection (N.C. 30) is also a triangular twin, but of a different type. It is much thicker, and also much more "like a crystal", that is to say the faces are much flatter and the edges much steeper than in the Panna examples. Examination of this specimen reveals the remarkable fact that its two faces and also the edges up to a third

of the way down from each face exhibit a close similarity to the Haidinger form of diamond. We have the same triangular faces with terraces, the same steep grooves below them and the same set of four sharp edges in the valence planes meeting near the vertices of the form. These features are incompatible with the usual description of the triangular diamonds as "spinel twins" obtained by cutting an octahedron in two and rotating one half through 180°. On the other hand, the specimen does exhibit in the vicinity of its median plane, the characteristic features of the form obtained in that way. It may accordingly be described as a remarkable but only partially successful attempt by a crystal of the tetrahedral class to mimic one of the characteristic forms of octahedral symmetry.

10. Some Descriptive Notes

In the paper by Ramaseshan in the 1944 symposium, descriptions, drawings and photographs have already been given of several of our Panna diamonds. There is little need for reproducing the same or similar material here, especially as the numerous figures in the text of the present paper represent the theoretical counterparts of the features described in the earlier one. Since, however, several additions have been made to our collection, some of which are of special interest, it appears desirable to include descriptive notes and illustrations of a few of the new acquisitions.

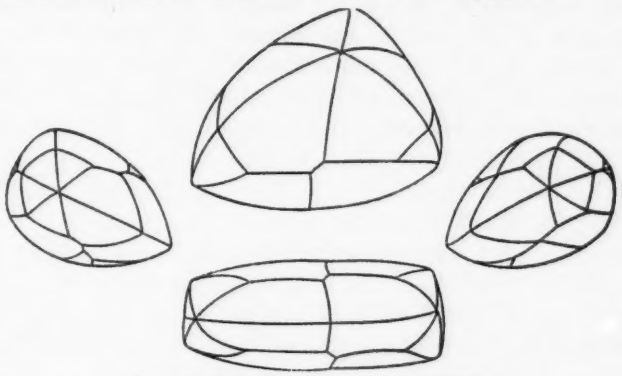


Fig. 12. *Front and Side views of N.C.* 14

N.C. 14.—This diamond from Maharajpur (Panna) weighs 143 milligrams, and is water-white in colour, but exhibits a faint greenish surface tinge of the kind which is fairly common in the Panna diamonds. This is the specimen in our collection which makes the nearest approach in its shape to the regular hexakis-tetrahedron of geometric crystallography and hence most clearly demonstrates that diamond is a crystal of the

tetrahedral symmetry class. The form is obviously lacking in a centre of symmetry. The eight triad vertices of the form fall into two groups of four each; in one group of four vertices, the edges meet accurately, and on the ridges connecting these vertices appear the six dyad vertices of the form. The other triad vertices appear on the four nearly flat faces of the form. In these vertices, the edges fail to meet and give rise to a pattern of broken lines as illustrated in Fig. 8 on an earlier page. Two of the triad vertices of the former group appear as pointed triangular tips at which three prominent ridges and three fainter ones midway between them meet. These tips are connected by an elongated ridge. The two other triad vertices of the same group are less prominent and are connected by a much shorter ridge, and the dyad vertex appearing midway between them is a prominent feature of the form. As a consequence of these features, both the general shape of the diamond and the details observed on it show only two of the planes of symmetry of the six which a perfect tetrahedron has. The two planes of symmetry are mutually perpendicular and contain between them all the eight triad vertices—four on each. Their intersection is a dyad axis of symmetry for the crystal.

N.C. 18.—This diamond from Udasna (Panna) weighs 57 milligrams and is perfectly water-white in colour. Being a relatively small diamond, the curvature of the faces is very marked. Nevertheless, the specimen shows clearly enough the characters of tetrahedral symmetry. The form lacks a centre of symmetry, and exhibits a trigonal axis at the two ends of which very different features are noticed. One end of the axis

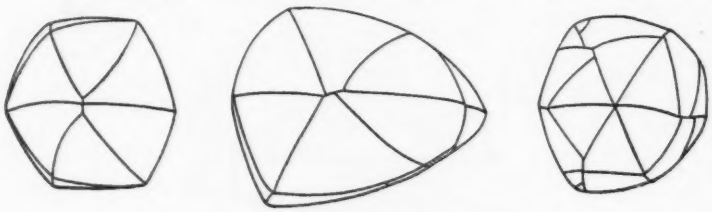


FIG. 13. *Front and End views of N.C.* 18.

is a sharp triangular tip where six edges meet. The other end is a nearly flat dome with a hexagonal perimeter bounded by three dyad and three triad vertices, all of which are fairly prominent. The four other triad vertices—appearing respectively on the triangular faces of the tip and on the dome at its end—are of a different description, being zig-zag patterns of broken lines. Three of the dyad vertices appear

on the ridges which converge towards the triangular tip of the form, and the three others around the base of the dome.

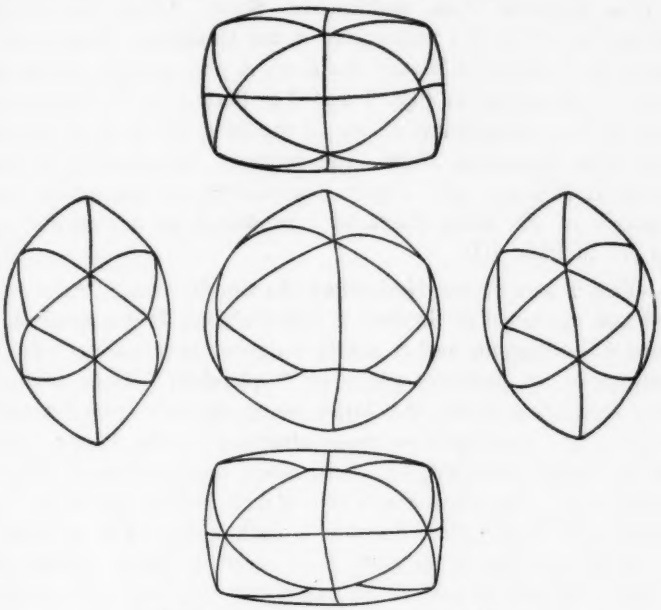


FIG. 14. *Front and Side views of N.C.* 10

N.C. 10.—This beautiful diamond from Maharajpur (Panna) weighing 182 milligrams, water-white in colour, with smooth lustrous faces, is well worthy of a detailed description as it illustrates a stage in the transition from the "tetrahedroid" to the "octahedroid" forms of diamond. The crystal exhibits a perfect symmetry of shape and of detail about two planes which are perpendicular to each other. These planes are two of the tetrahedral symmetry planes and the line along which they intersect is a dyad axis also for the actual shape of the crystal. The two ends of this axis are prominent dyad vertices of the form and exhibit the tetrahedroid character, appearing as ridges rather than as peaks. Since one of them is much more pronounced than the other, the crystal form has no centre of symmetry. The four other dyad vertices come next in order of prominence and are all exactly alike each other. They are peaks rather than ridges and thus exhibit an octahedroid character. The triad vertices form pairs, two of which appear in each of the two symmetry planes of the crystal. The four pairs of vertices are of progressively diminishing prominence. They illustrate the successive stages

of the transformation of a triad vertex from a perfect meeting of six ridges to an elongated zig-zag of broken lines.

N.C. 25—This diamond from Bultfontein, South Africa, water-white in colour and weighing 211 milligrams, is the Haidinger form already described in some detail in Section 8 above. A photograph with an accompanying sketch appear in Figs. 1 and 2 in Plate I of this paper. Fig. 10 in Plate III is a photograph of one of the faces of the form showing its characteristic hexagonal shape, the terraces surrounding it and the triangular depressions or " trigons " appearing on the same. Another photograph of the same diamond reproduced as a negative appears as Fig. 11 in Plate III.

N.C. 164.—This is one of the Hyderabad diamonds whose forms were described and explained in Sections 2 and 7 above. It is a small diamond weighing 62 milligrams and is nearly water-white in colour. It exhibits a combination of optically plane or " splendent " faces with curved surfaces separating them, the latter being smooth and lustrous and exhibiting edges analogous to those observed on the Panna diamonds. In this particular diamond, six of the plane faces are much larger than the other two. The photograph reproduced as Fig. 3 in Plate I shows the smallest of all the plane faces as a dark area. Fig. 9 in Plate III is an enlarged picture of the same face, showing clearly the curved surfaces surrounding it as well as the edges crossing them and meeting the vertices of the plane face. The sketch reproduced in Fig. 4 in Plate I shows in addition two of the larger plane faces of the diamond and the curved surface lying between them and separated into sections by a system of curvilinear edges. See also Fig. 12 in Plate III where the photograph is reproduced as a negative.

N.C. 26.—This diamond from South-West Africa, weighing 191 milligrams and water-white in colour, is the " rhombic dodecahedron" the features observed on which have been described and explained in Section 7 above. Photographs and sketches of it from two different points of view are reproduced as Figs. 5, 6, 7 and 8 in Plate II and in Figs. 13 and 14 in Plate III.

11. The Allotropic Modifications of Diamond

It is useful here to review our findings in so far as they have a bearing on the question of the symmetry of the internal structure of diamond. What the evidence indicates is that in the majority of the cases studied and possibly in all, the crystal symmetry is that of the tetrahedral class only and that none of the crystals appearing in our collection presents conclusive evidence of

its possessing a true octahedral symmetry. There is, however, a pronounced tendency towards the assumption of crystal forms which may be indifferently regarded as either tetrahedral or octahedral. This tendency would result from an interpenetration of positive and negative tetrahedral forms, and there is crystallographic evidence that such interpenetration does occur. But it should not be forgotten that the same situation would arise from the existence of diamond having a truly octahedral symmetry of structure but formed under conditions unfavourable for the intrinsic symmetry expressing itself to the fullest extent in the external form. The possibility has also to be borne in mind that the modifications of diamond having tetrahedral and octahedral symmetry of structure appear intertwinned with each other in the same crystal. In all such cases, we could scarcely expect the crystal forms to exhibit either tetrahedral or octahedral symmetry exclusively. It would then be necessary to rely on physical evidence, as for instance the infra-red absorption spectrum, to discriminate between the various possibilities and to establish the nature of any particular specimen.

Summing up the situation, we may say that while the study of the crystal forms in our collection shows clearly enough that the majority of diamonds have only a tetrahedral symmetry of structure, the results do not exclude the possibility that diamond has in some cases a truly octahedral symmetry of structure which for one reason or another fails to manifest itself fully in the external form of the crystal.

12. Summary

The paper describes the conclusions reached from a critical examination of some 72 diamonds in their natural form obtained from various sources. The curvature of the faces and other special features exhibited by diamond invalidate a description of its forms in the standard terminology of geometric crystallography. The proper basis for description and classification is furnished by the configuration of the sharply-defined edges which appear dividing the superficies of the crystal into 24 distinct sections. Subject to minor modifications, these edges lie along the intersections of the surface with the symmetry planes of a fundamental tetrahedron. These planes also contain the directions of the valence bonds between the carbon atoms in the crystal and the sharpness of the edges is determined by the angle which they make with the valence directions. The configuration of the edges and the specific features exhibited by them in numerous specimens prove that in the majority of diamonds the crystal symmetry is that of the tetrahedral class only. The crystallographic evidence also shows that the positive and negative tetrahedral forms freely interpenetrate each other, and this explains the

frequent appearance of forms common to the tetrahedral and octahedral symmetry classes. That diamond may in some cases possess a true octahedral symmetry is however entirely consistent with the observed facts. A physical theory of the formation of diamond is outlined which explains the observed features of the crystal forms and enables them to be classified in a regular sequence.

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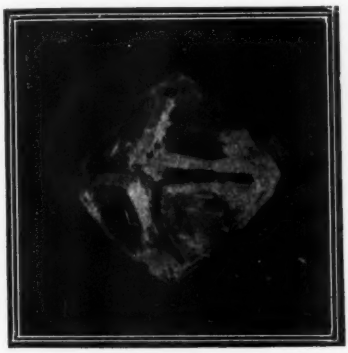

FIG. 1

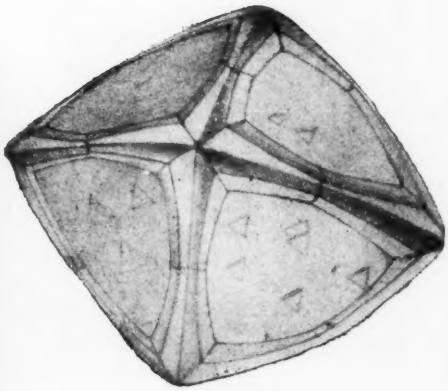

FIG. 2

Haidinger Diamond (N.C. 25)

FIG. 3

FIG. 4

Hyderabad Diamond (N.C. 164)

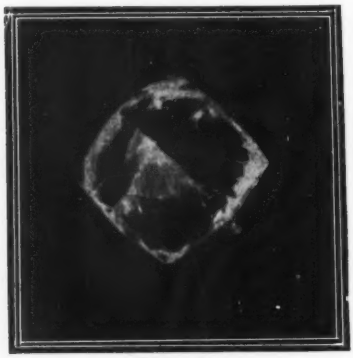

FIG. 5

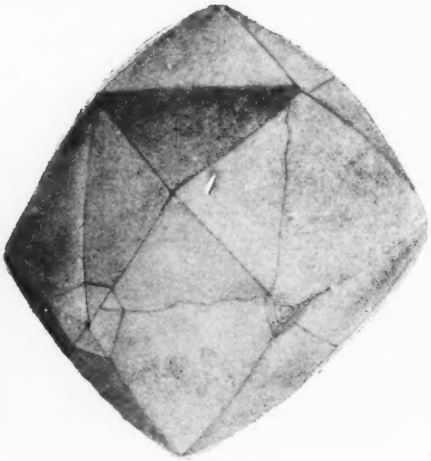

FIG. 6

N.C. 26

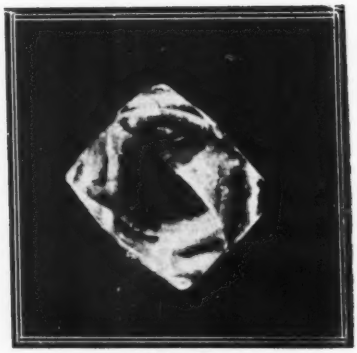

FIG. 7

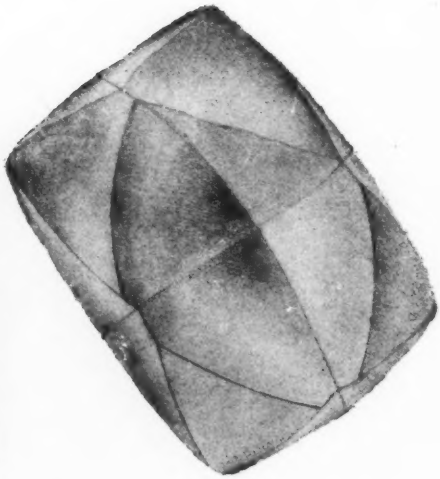

FIG. 8

N.C. 26

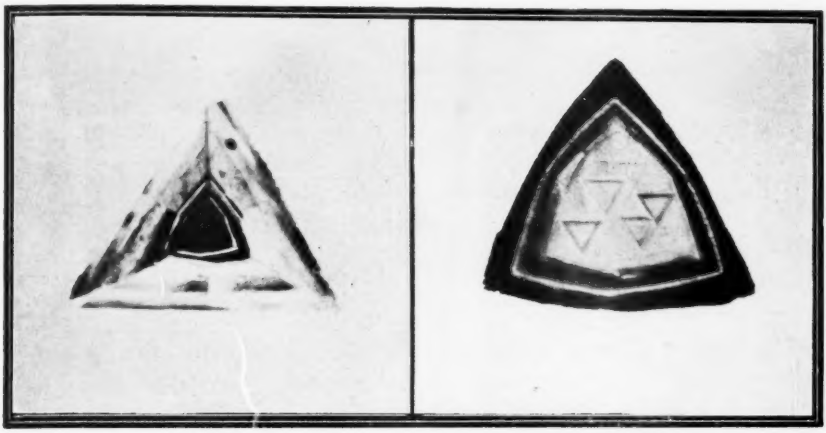

FIG. 9

FIG. 10

N.C. 164

N.C. 25

FIG. 11

FIG. 12

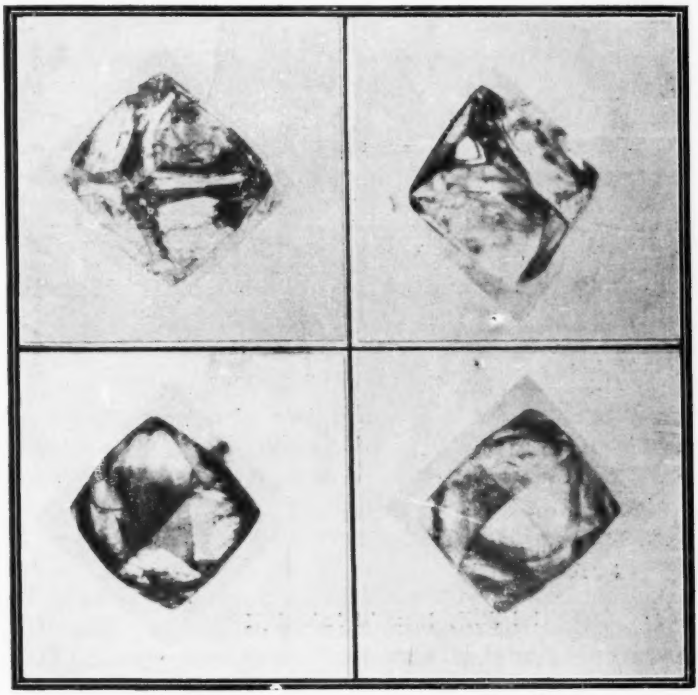

FIG. 13

FIG. 14

THE SECOND ORDER RAMAN SPECTRUM OF DIAMOND

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1. Introduction

The Raman effect in diamond has been studied by several investigators, *viz.*, Ramaswamy (1930), Robertson and Fox (1930), Bhagavantam (1930), Robertson, Fox and Martin (1934) and Nayar (1941, 1942). They reported the existence of only a single sharp and intense Raman line with a frequency shift of 1332 cm.$^{-1}$ corresponding to the triply degenerate vibration of the two Bravais lattices of carbon atoms with respect to each other. Investigations by Robertson, Fox and Martin (1936) on the infra-red absorption spectrum and those by Nayar (1941 *a*, 1942 *a*) and by Miss Mani (1944) on the luminescence and absorption spectra of diamond, however, indicated that the lattice spectrum includes many more vibrations with discrete frequencies besides the one with the frequency shift of 1332 cm.$^{-1}$ so far recorded in the Raman spectrum. It was therefore natural to expect that some of these vibrations would manifest themselves as second order Raman lines in an intensely exposed spectrum of diamond. Accordingly, the author (Krishnan, 1944) undertook a re-examination of the Raman effect in diamond. The technique of using the visible and near ultra-violet radiations of the mercury arc as exciter has been exploited to the limits of its utility by the investigators already referred to, and consequently no further useful information regarding the second order spectrum of diamond would be got by employing the same. Using the extremely intense 2536·5 mercury resonance radiation from a water-cooled magnet-controlled mercury arc as exciter and diamonds of the ultraviolet transparent type, the author succeeded in recording a spectrum which exhibited besides the intense line with a frequency shift of 1332 cm.$^{-1}$, no fewer than ten Raman lines of comparatively feeble intensity. These constitute the Raman spectrum of the second order in diamond, the appearance of which was predicted on the basis of the Raman dynamics of crystal lattices. In the preliminary investigation the results of which were published in the earlier symposium (Krishnan, 1944), the author had used a quartz spectrograph of small dispersion. Because of this and also due to imperfect reproduction, the second order Raman lines are not

seen clearly resolved from the background either in the spectrogram or in the microphotometric record. Using a Hilger medium quartz spectrograph which had a higher dispersion than the one previously employed, fresh photographs were obtained, the best of which was published in *Nature* (Krishnan, 1945). Here also the reproduction was not quite satisfactory, as the picture was too small to bring out the real nature of the second order Raman spectrum of diamond, *viz.*, a set of sharp lines appearing on a feeble continuum. It was therefore thought desirable to investigate the problem afresh under more favourable conditions. Improved experimental technique and the use of an exceptionally colourless plate of diamond belonging to the ultraviolet transparent type recently acquired by Sir C. V. Raman have enabled the author to record spectra of much greater intensity and much better resolved. The results are presented in this paper.

2. Experimental Details and Results

The catalogue number of the diamond used is N.C. 174. It was in the form of a semicircular disc about one centimetre in diameter and 2 millimetres thick. It was held with its flat faces vertical and facing the most intense portion of a specially designed quartz mercury arc. The arc was run under special conditions so as to emit the resonance radiation with exceptional intensity. The light scattered through the straight edge of the diamond was focussed on the slit of a Hilger (E3) medium quartz spectrograph. The diamond was kept cool with the aid of a fan. The scattering from the specimen was so intense that the principal line could be recorded on the plate with an exposure of five seconds, while an exposure of the order of one hour was sufficient to bring out the essential features of the second order spectrum. Numerous spectrograms were taken with exposures varying from 15 seconds to 15 hours. Kodak B 20 Process Regular plates were used. It is interesting to record the fact that the second order spectrum becomes visible with an exposure of 15 minutes and the anti-Stokes of the principal line 1332 cm.$^{-1}$ appears with an exposure of 45 minutes.

A microphotometric record of a moderately exposed spectrogram is reproduced together with the spectrum itself as Fig. 1 (*a*) and 1 (*b*) in Plate IV. The microphotometric record of the mercury arc is also included in Fig. 1 (*c*) for purposes of comparison. The photograph and the microphotometric record reproduced here represent a considerable improvement on the ones published earlier by the author. As is evident from the figures, the second order spectrum of diamond is mainly confined to a region extending to about 300 wave numbers on either side of λ 2698·9. It consists of a series of distinct Raman lines of which at least 7 can be dis-

tinguished without difficulty. Their positions have been marked in Fig. 1 (*a*). The frequency shifts of these lines have been accurately determined by direct measurements made on the negative. Their values are 2176, 2253, 2299, 2330, 2460, 2502 and 2666 cm.$^{-1}$ Three of them, namely the lines at 2176, 2460 and 2666 cm.$^{-1}$, stand out prominently in the spectrum. The line at 2460 cm.$^{-1}$ is the most intense one, while the sharpness of the line at 2666 cm.$^{-1}$ is comparable with that of a mercury line. The line at 2502 cm.$^{-1}$ has an appreciable width extending from 2490 to 2514 cm.$^{-1}$ This line can be seen clearly separated from the intense line at 2460 cm.$^{-1}$ See Fig. 1 (*b*). The line with the frequency shift 2253 cm.$^{-1}$ appears to have a finite width. A careful examination of a lightly exposed spectrogram and its microphotometric record has shown that this line is made up of two closely spaced lines with frequency shifts 2245 and 2265 cm.$^{-1}$

Besides the 7 lines described above, the presence of at least 3 other feeble lines with frequency shifts 2190, 2225 and 2430 cm.$^{-1}$ has been identified by a careful scrutiny of the spectrogram and its microphotometric record. The positions of these lines have also been indicated in Fig. 1 (*a*). The frequency shifts of the 10 Raman lines belonging to the second order spectrum are listed in Table I, those of the prominent lines being shown in heavy type.

TABLE I

Second Order Spectrum of Diamond

No.	Frequency shifts of the observed Raman lines in cm.$^{-1}$	Relative intensity	Frequencies of the observed infra-red absorption maxima in cm.$^{-1}$
1	**2176**	5	**2170**
2	**2190**		**2186**
3	**2225**		**2217**
4	**2253**	7	**2240**
5	**2299**	8	**2290**
6	**2330**	9	
7	**2430**		
8	**2460**	15	**2452**
9	**2502**	13	**2506**
10	**2666**	10	**2666***

* Please see remarks in text. The frequencies of the prominent peaks appearing in the infra-red absorption spectrum are also shown in heavy type.

Superposed over the Raman lines there is a feeble continuum which extends from the Raman line 2253 cm.$^{-1}$ to the line 2666 cm.$^{-1}$ It is to be remarked that the line with the frequency shift of 2666 cm.$^{-1}$ has an individual

existence and is not merely the sharp cut off of the continuum. See Figs. 1 (*a*) and 1 (*b*).

The values of the frequency shifts of the second order Raman lines reported earlier by the author were less accurate than the values presented now, as the former had to be evaluated from measurements made on the microphotometric record. In the region between the mercury triplet and λ 2675·0 there is a sharp Raman line separated by about 1940 wave numbers from λ 2536·5. See Figs. 1 (*a*) and 1 (*b*). This was wrongly assigned as a second order Raman line in the paper published in the earlier symposium. It should, however, be assigned as the first order Raman line 1332 cm.$^{-1}$ excited by the mercury line λ 2576·3. The Raman line at λ 2749 seen in Figs. 1 (*a*) and 1 (*b*) likewise corresponds to a first order line with the frequency shift 1332 cm.$^{-1}$ excited by the mercury line λ 2652.

3. Intensity Measurements

In order to estimate the relative intensities of the second order Raman lines as well as the ratios of the intensities of the Stokes, the anti-Stokes and the octave of the principal Raman line 1332 cm.$^{-1}$, the following procedure was adopted. As already mentioned in the last section, a series of photographs of the Raman spectrum of diamond was taken with exposures varying from 15 seconds to 15 hours. Standard developers were used throughout and the time and temperature of development was kept constant. A series of graded intensity marks was obtained on a separate Kodak B 20 plate by photographing the spectrum of a tungsten filament lamp provided with a quartz window with different slit-widths, but keeping the time of exposure constant. A second series of photographs was taken on another plate varying the time of exposure but keeping the slit-width constant. These two negatives were put through the microphotometer. With the aid of the microphotometric records, the density-log intensity and density-log time curves were plotted for the spectral region corresponding to the mean wave-length λ 2650. From these curves, the Schwarzschild correction factor appearing in the expression for the photographic density as exponent for time was evaluated. For λ 2650 the Schwarzschild factor has the mean value of 0·8.

With the help of the density-log intensity curve and the microphotometric record of a moderately exposed spectrogram of the Raman effect in diamond, the relative intensities of the prominent second order Raman lines were evaluated in the usual way. Taking the intensity of the line 2666 cm.$^{-1}$ as 10 arbitrary units, the intensities of the other lines have been calculated and the values are listed in Table I. It is reasonable to assume that the

intensities of the lines 2176, 2460, 2502 and 2666 cm.$^{-1}$ are not affected to any appreciable extent by the presence of the feeble continuum and hence the values given in Table I may be taken to represent the actual peak intensities of these lines.

With the aid of the microphotometer and using the series of photographs of the Raman spectrum taken with graded exposures, the density-log time curves were plotted for the Stokes line (1332 cm.$^{-1}$), the anti-Stokes line ($-$ 1332 cm.$^{-1}$) and the octave (2666 cm.$^{-1}$). The time of exposure required to produce the same density (darkening) on the plate by each one of these lines was read off from the respective density-log time curve. Knowing the values of the exposure time for the three lines, their relative intensities were evaluated using the known value of the Schwarzschild factor. For the 1332 Raman line in diamond, the ratio of the intensities of the Stokes to the anti-Stokes is 575, while that of the fundamental to the octave is 290. In evaluating the former ratio it has been assumed that the density-log intensity curve is the same for the two regions of the spectrum, namely 2625 A.U. and 2453 A.U. where the Stokes and anti-Stokes lines fall.

The ratio of the intensity of the Stokes to that of the anti-Stokes line to be expected on the basis of the Boltzmann formula was evaluated taking the temperature of the diamond to be 27° C. It is equal to 590 which agrees fairly well with the observed value of 575.

4. Infra-Red Spectrum of Diamond

The infra-red absorption spectrum of diamond was investigated in some detail by Robertson, Fox and Martin (1934). They reported the existence of three distinct regions of absorption in diamonds of the ultra-violet opaque type and two in diamonds of the transparent type. The three groups of absorption which were denoted by letters A, B and C appeared respectively at 3 μ, 4–4·8 μ and 7–9 μ. They could not detect any difference in the structure of the absorption bands given by the two types of diamond except for the absence of the absorption band C in diamonds of the ultra-violet transparent type. Robertson, Fox and Martin analysed the absorption in the region from 4–4·8 μ into three separate absorption bands denoted by the letters B′, B_α and B_β. They noticed definite indications of structure in the absorption bands B_α and B_β. See Fig. 7 reproduced on page 482 of their paper.

Two years later, Robertson, Fox and Martin (1936) carried out further exploration of the fine structure of the absorption bands B_α and B_β with the aid of a grating. The absorption curve obtained thereby is reproduced in Fig. 1 (*a*) on page 581 of their second paper. The B_α band is bounded on

either side by a steep fall in absorption strength and exhibits a very sharp and prominent peak on its longer wavelength edge which forms a characteristic feature of this absorption band. Robertson, Fox and Martin gave the value of 2170 cm.$^{-1}$ for the frequency of infra-red vibration corresponding to this peak. This peak may be identified in its position with the Raman line 2176 cm.$^{-1}$ which stands out prominently in the observed second order spectrum.

The principal peak at 2170 cm.$^{-1}$ is followed by two others, then by a well-deftned kink and finally by another peak. The positions of these have been estimated by the author from the curve reproduced by Robertson, Fox and Martin (1936) and their values in wave numbers are 2186, 2217, 2240 and 2290. These are included in Table I. The positions of these peaks and kinks may be identified with those of the observed Raman lines 2190, 2225, 2253 and 2299 cm.$^{-1}$ Thus the fine structure of the infra-red absorption band B_α shows a very striking correspondence with the features observed in the second order spectrum.

Robertson, Fox and Martin (1936) re-examined the absorption band at $4{\cdot}1\,\mu$ also with the aid of a grating, but no new details except those already reported by them in their earlier paper were obtained. In the absorption curves of the two types of diamond reproduced in Fig. 7 on page 482 of their paper, the band at $4{\cdot}1\,\mu$ exhibits some structure. The existence of two rather broad peaks is easily noticeable in the absorption band of the ultra-violet transparent type of diamond. The positions of these have been estimated by the author. Their frequencies in wave numbers are 2452 and 2506 cm.$^{-1}$ Corresponding to these two infra-red absorption maxima, one observes two intense Raman lines with frequency shifts 2460 and 2502 cm.$^{-1}$ appearing prominently in the second order spectrum.

The absorption curve for diamond of the ultra-violet opaque type shows a peak coinciding with the fundamental Raman frequency of 1332 cm.$^{-1}$ (K. G. Ramanathan, 1946, see the paper appearing elsewhere in this symposium). The fine structure of the corresponding absorption band in the $4{\cdot}1\,\mu$ region has not been investigated. The curve reproduced by Sutherland and Willis (1945), however, shows a precipitous fall of absorption strength beyond the $4{\cdot}1\,\mu$. The point where the slope is greatest has the same frequency as that of the Raman line of frequency shift 2666 cm.$^{-1}$

5. Comparison with Luminescence and Absorption Spectra

The luminescence and absorption spectra of diamonds have been studied in great detail by Nayar (1941 *a*, 1942 *a*) and by Miss Mani (1944). Associated with the principal electronic lines at λ 4152 and λ 5032 a set of lattice

lines appears at greater wavelengths in fluorescence and at diminished wavelengths in absorption. The most clearly defined and prominent lattice frequencies appearing in luminescence and absorption spectra are in wave numbers 1332, 1251, 1149 and 1088. The Raman lines with frequency shifts 2666, 2502, 2299 and 2176 cm.$^{-1}$ appearing prominently in the second order spectrum are evidently the octaves of these lattice frequencies.

6. Conclusion

According to the existing theories of Debye and Born, the vibration spectrum of a crystal is essentially a continuous distribution of frequencies ranging from zero upwards. On this basis, the appearance of only a single sharp and intense line with the frequency shift of 1332 cm.$^{-1}$ in the Raman spectrum of the first order in diamond is scarcely intelligible. In order to get over this obvious contradiction with the facts, it has been suggested that only the limiting frequencies of the lattice, *viz.*, those having phase-wavelengths large compared with the lattice spacing could appear in the observed Raman spectrum. It is further assumed that the frequencies of the vibrations of shorter phase-wavelengths disappear by reason of the optical interference of the effects due to them arising from different volume elements. There is no experimental justification for such an assumption. Even if it were valid, the second order spectrum of diamond should likewise consist of a single sharp line corresponding to the octave of the limiting frequency of vibration, namely 2664 cm.$^{-1}$ What is actually observed is wholly different, *viz.*, a set of Raman lines with discrete frequencies. It is therefore impossible to reconcile the consequences of the Born theory with the experimental facts of the Raman effect in diamond.

The appearance of a set of lines with discrete frequency shifts in the second order spectrum of diamond finds a natural explanation in the new theory of lattice dynamics put forward by Sir C. V. Raman (1943). According to the Raman dynamics the diamond lattice has a small number of fundamental modes of vibration with discrete frequencies. The observed second order lines are the octaves and allowed combinations of some of these fundamental frequencies of oscillation of the diamond lattice.

The author is grateful to Professor Sir C. V. Raman for the loan of the diamond used in the present investigation and for some useful discussions.

7. Summary

Using an exceptionally colourless plate of diamond of the ultra-violet transparent type and the λ 2536·5 resonance radiation of mercury as exciter, the author has photographed the second order Raman spectrum of diamond

with greatly increased intensity and much better resolved than any recorded hitherto. The spectrum exhibits ten distinct Raman lines with frequency shifts 2176, 2190, 2225, 2253, 2299, 2330, 2430, 2460, 2502 and 2666 cm.$^{-1}$ The frequency shifts of the first five lines, in particular, correspond very closely with the positions of a set of five absorption peaks observed by Robertson, Fox and Martin while exploring the absorption band in the region 4–4·8 μ with the aid of a concave grating of the echelette type. Of the ten observed second order Raman lines, the more intense and prominent ones have been identified as octaves of the prominent lattice frequencies of diamond appearing in the luminescence and absorption spectra. These facts are irreconcilable with the consequences of the Born lattice dynamics. They can, however, be satisfactorily explained on the basis of the Raman dynamics of crystal lattices.

The relative intensities of the second order Raman lines, as well as the ratios of the intensities of the Stokes, the anti-Stokes and the octave of the principal Raman shift of 1332 cm.$^{-1}$ have been estimated by photographic photometry.

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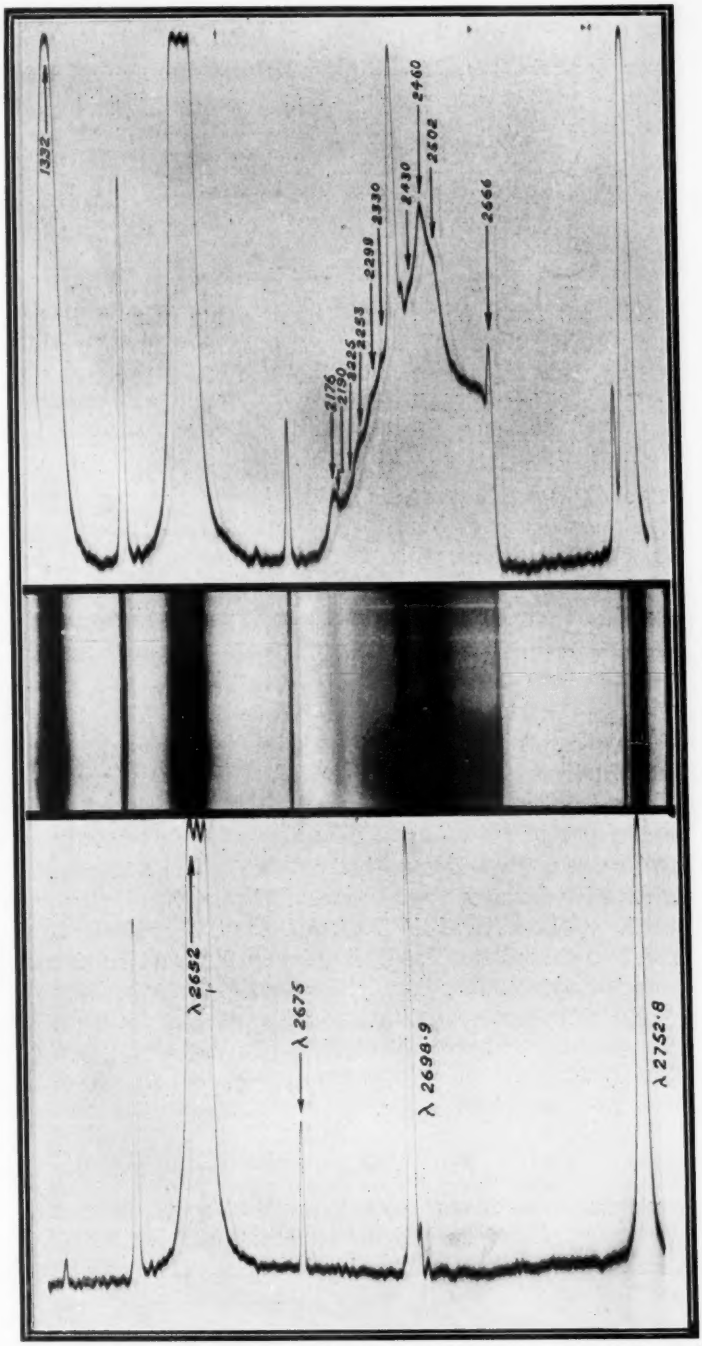

FIG. 1. (*a*) Microphotometer record of the second order spectrum of diamond.
(*b*) The Raman spectrum of the second order in diamond.
(*c*) Microphotometer record of the mercury spectrum.

THERMAL EXPANSION OF DIAMOND

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1. Introduction

It is well known that the coefficient of thermal expansion of a solid behaves qualitatively in the same manner as the specific heat, becoming constant at high temperatures, but reducing to zero as the temperature approaches the absolute zero. Grüneisen (1912) who was the first to draw attention to this fact derived the following relation connecting the coefficient of thermal expansion α and the specific heat C_v of simple solids:—

$$\alpha = \frac{\gamma \chi_0 C_v}{V_0}, \qquad (1)$$

where χ_0 = the compressibility

V_0 = the atomic volume

and γ = a constant independent of temperature.

Taking the value of γ as 1·1 for diamond and its specific heat values as given by a single Debye function corresponding to a characteristic temperature of 1860, Grüneisen (1926) satisfactorily explained the existing data on the thermal expansion of diamond due to Röntgen (1912) which covered the range of temperature from 84° T. to 350° T. Although the Grüneisen's relation is found to be valid over this range, a satisfactory test of the relation should require data over a wider range of temperature. Accurate measurements of the heat capacity of diamond have already been made by Pitzer (1938) over the range of temperature from 70° T. to 300° T. and by Magnus and Hodler (1926) from 273° T. to 1100° T., while the thermal expansion of diamond does not appear to have been investigated above 350° T. In view of the importance of the Grüneisen's relation in the theory of the solid state and its bearing on the nature of the vibration spectrum of a crystal, it was considered desirable to obtain data on the thermal expansion of diamond in order to test the validity or otherwise of the Grüneisen's relation for diamond at high temperatures. In the present investigation* the thermal

* A preliminary report of the measurements of the coefficient of thermal expansion of diamond made by the author over the range of temperature from 28° to 680° C. appeared in *Nature* (Vol. 1944, 154, 486). The results obtained definitely established the dependence of γ on the temperature. The present paper deals with the results of new and more accurate measurements made by the author.

expansion of diamond has been studied over the range of temperature from 300° to 873° T.

2. Technique of Study

As the expansion of diamond is rather small compared with that of ordinary solids and as the specimens available for study were in the form of thin plates, direct determination of the thermal expansion by the interferometric method could not obviously be made with any reasonable degree of accuracy. The X-ray diffraction method was therefore employed and the variation of lattice spacings with increase of temperature was measured and the coefficient of thermal expansion calculated. The technique of study was rather different from that usually adopted, being designed to enable the small expansion of diamond to be measured accurately. It was based on the use of a beam of characteristic X-rays from a copper target diverging from a fine slit and falling on the crystal nearly at the Bragg angle for surface reflection. The photographic film recording the reflections was kept at a considerable distance from the latter. With a perfect crystal like some specimens of diamond, the characteristic X-ray reflections would appear as sharp lines, the width of which being nearly independent of the distance of the film from the crystal, would be determined by the fineness of the slit used. From the observed displacements of the $CuK\alpha_1$ and $K\alpha_2$ reflections when the temperature of the crystal was raised, the relative change in crystal spacing could be evaluated. The observed shift being directly proportional to the crystal-film distance, a very high degree of accuracy could be attained by increasing the latter.

3. Description of Apparatus

Camera.—Fig. 1 represents a horizontal cross-section of the X-ray camera employed in the present investigation. It consisted of a fine lead slit S (4 mm. high and 0·09 mm. wide) which was kept facing and close to the window of a Coolidge demountable X-ray tube provided with a copper target. At a distance of about 5 cm. from the slit was placed a single circle goniometer G. The goniometer was so adjusted that its vertical axis was accurately parallel to the height of the slit. To the axial rod of the goniometer was fixed a fused quartz tube with a drawn out end. The crystal to be examined was held firmly in a slot at the drawn out end. The quartz tube was long enough to ensure that its lower end was not sensibly heated up while the crystal itself was raised to the desired temperature by being enclosed in a small electrically heated chamber or furnace. The latter which is not shown in Fig. 1 formed a separate unit which could be lowered over the crystal after all the necessary settings and adjustments have been made. To

the lower end of the goniometer axis were fixed two wooden arms about a meter in length, each one subtending an angle $2\theta_B$ with the line joining the slit to the crystal (see Fig. 1). θ_B is the Bragg angle for 111 reflection of diamond using CuKα radiations and has the value 21° 58′. Each arm carried a film holder (F_1 and F_2) which could be clamped at any desired distance from the crystal. The films were always kept normal to the reflected beam. A Hartmann diaphragm H provided with three holes was supported in front of each film holder as shown in the figure. With the aid of this diaphragm three sets of X-ray reflections could be recorded in juxtaposition on the same film.

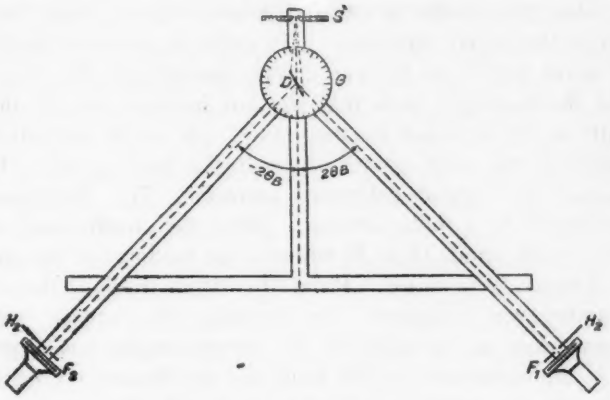


FIG. 1. X-Ray Camera

The Furnace.—The constant temperature chamber consisted of a thin steel cylinder about 2½″ long and ½″ bore. In order to permit free passage of X-rays over a wide angle through the centre of the heater, two segments about ¼″ high were cut away from the centre of the tube leaving two narrow ribs connecting the top and bottom halves of the tube. To improve the uniformity of temperature within the chamber these segments were then closed by pieces of extremely thin aluminium foil (0·007 mm. thick). The steel part of the tube was covered with a mica sheet and the heating coil was wound over the mica and set in position with the aid of a mixture of alumina and sodium silicate solution and finally covered over with asbestos. Thick aluminium foil was then stuck on the outside of the furnace in order to minimise heat losses due to radiation. The top of the furnace was closed by an iron disc to which was screwed a thin metal tube. The latter was cemented on to a pyrex glass tube which was in turn fixed to the adjustable arm of a vertical stand. After placing the furnace in position above the crystal, it could be lowered vertically into the right position by means of a

rack and pinion arrangement. The orifice at the bottom of the tube was partially closed by the quartz tube which supported the diamond to be studied. The furnace had a low heat capacity so that the required temperature could be reached within a conveniently short time.

4. Details of the Experiment

Calibration of the Furnace.—As it was not possible to have a thermocouple inside the furnace to record the temperature of the crystal during exposures, the constant temperature chamber was calibrated beforehand. A calibrated nichrome constantan thermocouple was supported vertically through a silica tube similar in size and shape to the one used for supporting the crystal in the actual experiment. In order to measure the temperature of the air space within the furnace it was lowered over the silica tube containing the thermocouple such that the hot junction was at the position subsequently to be occupied by the crystal. A steady current from a set of accumulators was then passed through the heating coil. The current was measured on a good calibrated ammeter. The thermocouple was directly connected to a millivoltmeter. When the steady state was reached which usually took about 15 to 20 minutes, the readings of the ammeter and the millivoltmeter were noted. From the latter reading, the temperature of the chamber was evaluated. On removing the furnace and replacing it, the temperature as recorded by the thermocouple was reproduced to $\pm$ 1° C. As the temperature of the leads had no influence on the temperature recorded by the hot junction, it can be assumed that the thermocouple recorded the true temperature of the air space inside the furnace. The experiment was repeated with various heating currents and the steady temperature attained in each case was noted. A curve showing the relation between the heating current and the steady temperature inside the furnace up to 650° C. was drawn. The furnace was recalibrated after a set of experiments and it was found that the calibration curve remained unaffected even after a lapse of six months. From the calibration curve the values of the heating current correct to the nearest readable division on the ammeter for temperatures as close to 100°, 200°, 300°, 400°, 500° and 600° C. as could conveniently be arranged were read off. The steady temperatures corresponding to these values of the heating current were accurately determined by experiment. They were 105°, 205°, 300°, 405°, 505° and 605° C. While measuring the variation of the lattice spacings the crystal was maintained successively at these temperatures.

Selection and Mounting of the Diamond.—As already remarked in Section 2, in order to attain a high degree of accuracy in the measurement

of the change of lattice spacing with temperature, it is necessary to use a piece of diamond which is the nearest approach to the perfect crystal. Recent measurements of Ramachandran (1944) on the angular divergence of X-ray reflections in different diamonds have shown that diamonds which are opaque to the ultra-violet and which exhibit least fluorescence have the least angular divergence the value of which is just a little more than that for an ideal crystal. Accordingly, diamond (N.C. 76) which had these characteristics was selected for the present investigation from Sir C. V. Raman's personal collection. It was in the form of a triangular plate, about 0·9 mm. thick, with its faces parallel to the octahedral cleavage planes.

The mounting of the diamond on a suitable support presented some difficulty. It was necessary to make the mounting sufficiently robust to withstand temperature changes without an accompanying change in the setting of the diamond. Any displacement of the diamond caused by the yielding of the support when the temperature of the latter was raised would produce a spurious shift of the X-ray reflection. After some trials, it was found that the use of a fused quartz tube for supporting the diamond and of a silicate dental cement for mounting it completely eliminated spurious effects up to a temperature of 500° C. In the range of temperature from 500° to 600° C. there was a slight effect which was corrected for by taking photographs of the X-ray reflections by rotating the crystal holder by twice the Bragg angle.

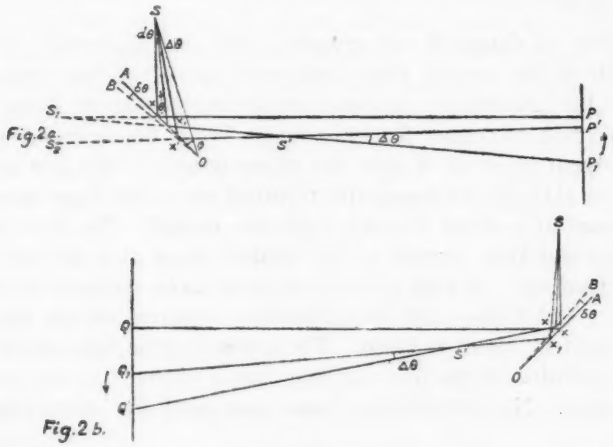
The plate of diamond was mounted such that its surface (111) planes were exactly in the vertical plane and were parallel to the vertical axis of rotation of the goniometer. It was then set roughly at the Bragg angle for surface reflection of copper Kα radiations. When the diamond was bathed in the divergent beam of X-rays, the characteristic CuKα line appeared in the distorted (111) X-ray topograph recorded on a film kept normal to the incident beam at a short distance from the crystal. The film holder was moved away and kept normal to the incident beam at a distance of 80 cm. from the diamond. A trial photograph was taken without the Hartmann diaphragm. The CuKα_1 and Kα_2 reflections appeared on the film as sharp lines separated by about 0·9 mm. The exposure time was adjusted so that the image recorded on the film was just clearly visible. It was of the order of 10 minutes. No intensifying screen was used for photographing the reflections.

Using the Hartmann diaphragm, three sets of X-ray reflections were recorded in juxtaposition on the same film, the middle one with the diamond heated up to a known temperature and the top and bottom ones as controls

at room temperature. The room temperature photographs were taken one before and the other after the high temperature exposure. During the experiment the camera was not disturbed. The goniometer was then turned through twice the Bragg angle, *i.e.*, 43° 56′, so that reflections could occur at the second face of the diamond. With this setting and keeping another film at a distance of 80 cm. from the crystal (see Fig. 1), a series of three photographs were recorded in juxtaposition on it, the middle one with the diamond heated up to the same temperature as before and the top and bottom ones as controls at room temperature. In this manner the experiment was repeated for temperatures 205°, 300°, 405°, 505° and 605° C. As the shift of the X-ray reflection was smaller than the width when the temperature of the crystal was raised from 28° to about 100° C., it was evaluated in the following way. First the shift due to the rise of temperature from 28° to 300° was determined followed by that due to the rise of temperature from 105° to 300° C. The difference gave the displacement due to an increase of temperature from 28° C. to 105° C. The X-ray films were measured under a cross slide micrometer.

5. Calculation of the Thermal Expansion Coefficient

When the temperature of the crystal is raised, its setting with reference to the camera might get altered giving rise to a spurious displacement of



Figs. 2 *a* & 2 *b*

the X-ray reflection. The observed shift would therefore be the sum of the displacement due to the change in the Bragg angle caused by the increase

in lattice spacing and the spurious displacement due to the change in the setting of the crystal. By taking measurements for two different goniometer settings as described in the previous section, the spurious effects are easily eliminated.

S is the slit and OA the front surface of the diamond in the first setting. At the room temperature the reflection appears at P or Q on the film (see Figs. 2 *a* and 2 *b*). S_1 is the image of S in the plane of the diamond. When the temperature is raised by $t°$ C., let the change in the lattice spacing be dl and the corresponding change in the *Bragg angle* $d\theta$.

$$\text{since } 2l \sin\theta = \lambda, \quad d\theta = \frac{dl}{l} \tan\theta. \tag{2}$$

This would produce a displacement x of the X-ray reflection on the photographic film. x is equal to $(R + L)\, d\theta$, where R and L are the distances of the crystal from the slit and the film respectively. Provided the setting of the crystal remains unchanged, the reflection will appear at P_1 and Q_1 for the two goniometer settings such that $PP_1 = QQ_1 = x = (R + L)\, d\theta$ (see Figs. 2 *a* and 2 *b*).

Let us suppose that at the higher temperature the setting of the crystal with reference to the camera is altered. Any vertical movement of the crystal in its own plane caused by the expansion of the support will not affect the horizontal displacement of the X-ray reflection. Rotation of the plate about a vertical axis and/or a displacement normal to itself would, on the other hand, adversely affect the observed shift of the X-ray reflection. Let us suppose that the diamond rotates through an angle $\delta\theta$ about the point 0 in the direction indicated in Figs. 2 *a* and 2 *b*. A reference to the two figures shows at once that the displacements of the X-ray reflection for the $+\theta_B$ and $-\theta_B$ settings are given by x_1 and x_2,

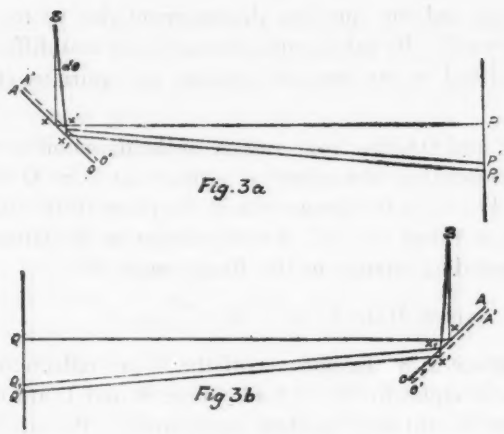
where $$x_1 = (L + R)\, d\theta - (L - R)\, \delta\theta$$

and $$x_2 = (L + R)\, d\theta + (L - R)\, \delta\theta.$$

$$\therefore \quad x = \frac{x_1 + x_2}{2} = (L + R)\, d\theta$$

Thus the mean value of x_1 and x_2 gives the actual displacement due to the change in the Bragg angle.

Similar results are also obtained for any displacement of the diamond normal to itself (see Figs. 3 *a* and 3 *b*). It will be noticed that the displacements of the X-ray reflection due to the rotation or displacement of the diamond are in the same sense for both the settings while those due to the lattice spacing variation are in opposite directions for the two settings.



FIGS. 3 *a* & 3 *b*

Let x_0 be the separation of $K\alpha_1$ and $K\alpha_2$ reflections. Then

$$x_0 = (L + R)\frac{d\lambda}{2l\cos\theta}.$$

where l = the lattice spacing and $d\lambda$ is the wavelength separation of $CuK\alpha_1$ and $CuK\alpha_2$.

$$\frac{x}{x_0} = \frac{d\theta \cdot 2l\cos\theta}{d\lambda}. \tag{3}$$

From equations (2) and (3) we get

$$\frac{x}{x_0} = \frac{dl}{l}\cdot\frac{\lambda}{d\lambda}. \tag{4}$$

The increase in lattice spacing dl for a rise of temperature of $t°$ is given by

$$dl = l \cdot \frac{x}{x_0}\frac{d\lambda}{\lambda} \tag{5}$$

and the mean coefficient of linear expansion is given by

$$\frac{\alpha}{3} = \frac{1}{t}\cdot\frac{dl}{l} = \frac{1}{t}\cdot\frac{x}{x_0}\cdot\frac{d\lambda}{\lambda}. \tag{6}$$

Thus the final expression for the coefficient of thermal expansion involves a term $\frac{x}{x_0}$ which could be accurately measured, λ the mean wavelength of the $CuK\alpha$ doublet and $d\lambda$ the wave-length separation. The values of λ and $d\lambda$ have been accurately determined by the earlier workers. The expression for α does not, however, involve the distance of the film from the crystal or the slit.

6. Results

Typical photographs of the X-ray reflection showing the progressive displacement of the lines as the temperature is raised are reproduced in Plate V.

TABLE I

Temperature Range °T.	Setting $(+\theta_B)$ $\frac{d_1}{x_0}$	Setting $(-\theta_B)$ $\frac{d_2}{x_0}$	Mean shift $\frac{d_1+d_2}{x_0} = \frac{x}{x_0}$	Change in lattice constant $da \times 10^3$
301–478 ..	·133	·131	·132	1·17 Å. U.
301–573 ..	·241	·239	·24	2·13
301–678 ..	·382	·375	·378	3·35
301–778 ..	·534	·512	·523	4·64
301–878 ..	·707	·652	·68	6·2
378–573 ..	·197	·193	·195	1·73
301–378 ..	·044	·046	·045	0·4

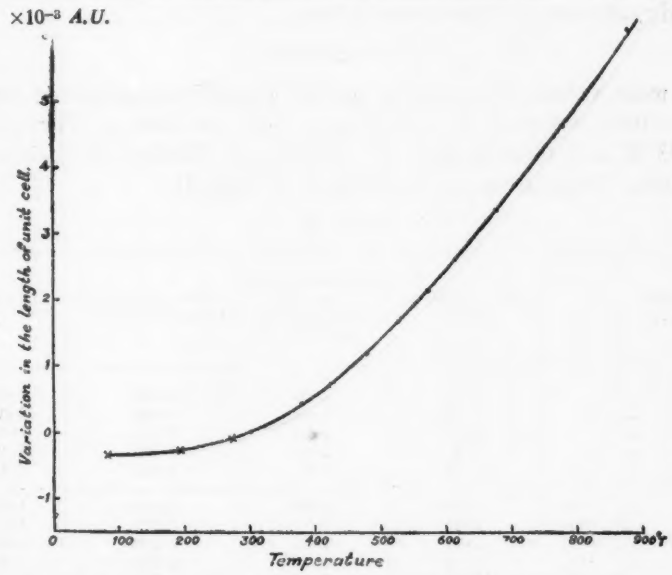


FIG. 4. Change of lattice constant as a function of temperature. Dots are author's values, and crosses are those calculated from the data of Röntgen

Table I gives the values of the displacements of the X-ray reflections in terms of the separation x_0 of the $K\alpha_1$ and $K\alpha_2$ lines. As already indicated in Section 4, the displacements of the reflections are nearly the same for both the settings of the goniometer up to a temperature of 505° C., *i.e.*, 778° T. The

increase of lattice-constant is calculated using equation (5) for the different temperature ranges and the values are given in column 5 of Table I. The lattice constant a at room temperature, *i.e.*, at 18° C. (291° T.) is taken as 3·55970 Å.U. The wave-lengths of $CuK\alpha_1$ and $CuK\alpha_2$ are taken as equal to 1·537395 and 1·541232 Å.U. respectively. In Fig. 3 the temperature of the diamond is plotted against the change of lattice-spacing taking the value at 28° C. (301° T.) as the standard. The portion of the curve below 301° T. was drawn using the data on the thermal expansion coefficients for this region recorded by Röntgen (1912) and quoted by Grüneisen (1926).

Mean coefficient of cubic expansion (α) over the ranges of temperature of about 100° has been evaluated using equation (6). The results are shown in the 3rd column of Table II. Those above the dotted line are taken from the determinations of Röntgen (1912). The curve showing the variation of the mean coefficient of volume expansion with temperature is reproduced in Fig. 4. The coefficient increases rapidly in the beginning and finally tends to a steady value at very high temperatures.

7. Discussion

The mean values of the atomic heat for the different ranges of tempera ture have been obtained by interpolation from the data of Pitzer (1938) below 273° T. and from the data of Magnus and Hodler (1926) above that temperature. These are given in column 5 of Table II.

Table II

Temperature Range °T.	$\frac{x}{x_0}$	Mean value of $\alpha \times 10^6$	Calculated values of α using Grüneisen's value for γ	Mean value of Atomic Heat C_v	$\gamma = \frac{\alpha V_0}{\chi_0 C_v}$
84·8–194·1 ..		0·54	0·50	0·233	1·19
194·1–273·2 ..		1·74	1·86	0·866	1·03
273·2–296·2 ..		2·91	2·91	1·351	1·10
296·2–328·1 ..		3·51	3·45	1·605	1·12
328·1–351·1 ..		4·35	4·02	1·870	1·19
301–378 ..	·045	4·36	4·08	1·870	1·20
378–478 ..	·087	6·51	5·8	2·627	1·27
478–573 ..	·108	8·52	7·55	3·307	1·31
573–678 ..	·138	9·84	8·78	3·874	1·30
678–778 ..	·145	10·86	9·47	4·329	1·28
778–878 ..	·157	11·76	10·03	4·657	1·29

Using the observed values of C_v and those of the coefficient of thermal expansion in equation (1), the values of γ for the different ranges of temperature have been evaluated. These are given in column 6 of Table II. The atomic volume V_0 is taken as equal to 3·42. The value of χ at 0° T. is not

known. The value of χ at 20° C. given by Adams (1921) as $0{\cdot}16 \times 10^{-12}$ cm.²/dyne has been used in the evaluation of γ. The difference between χ_{293} and χ_0 would be very small for a crystal of extremely low compressibility like diamond. The results presented in Table II go to show that γ, far from being independent of temperature, varies with temperature. Its value increases steadily from about 1·03 in the temperature range 194–273° T. to 1·31 in the range 478–573° T. Above this temperature the value decreases slowly.

Taking γ to be independent of temperature and equal to 1·1 as suggested by Grüneisen, Saksena (1944) has calculated the thermal expansion coefficients

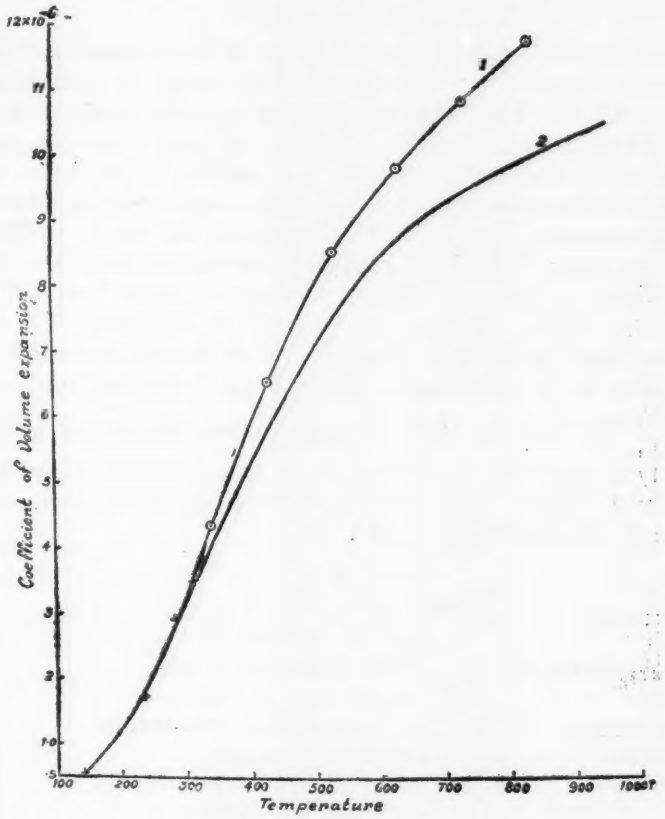


FIG. 5. Mean coefficient of expansion as a function of temperature
Curve 1: Experimental ; Curve 2: Theoretical on the basis of $\gamma = 1{\cdot}1$

of diamond for different ranges of temperature using equation (1). His results are given in column 4 of Table II. The variation of the thermal expansion coefficient with temperature to be expected on the basis of Grüneisen's relation is graphically represented by curve 2 in Fig. 5. There is fairly good agreement between the observed and calculated values of the coefficient of thermal expansion in the lower ranges of temperature, whereas at the higher temperatures the observed values are definitely higher, *e.g.*, to the extent of about 18% at about 600° C.

The author wishes to express his grateful thanks to Sir C. V. Raman for the loan of the diamond and also for his kind interest in the work.

8. Summary

Using the X-ray method, the change in the lattice spacing of diamond with temperature has been measured over the range of temperature from 28° C. to 605° C. The technique employed is rather different from that usually adopted, being designed to enable the rather small expansion of diamond to be measured accurately. The increase in the lattice constant at ordinary temperatures is small, while it is very rapid at higher temperatures. From the observed changes in lattice constant, the mean coefficients of volume expansion for different ranges of temperature have been deduced. The coefficient of volume expansion of diamond varies from $4{\cdot}36 \times 10^{-6}$ in the range 301° – 378° T. to $11{\cdot}76 \times 10^{-6}$ in the range 778°–878° T. Using the observed values of the coefficient of thermal expansion and the existing data on the atomic heat, the Grüneisen's constant γ which is the ratio $\frac{\alpha V_0}{\chi_0 C_v}$ has been evaluated. V_0 is the atomic volume and χ_0 the compressibility of diamond. It is shown that γ is not a constant, but increases from about 1·1 at low temperatures to about 1·3 at 600° T. and falls again slowly as the temperature is raised. .

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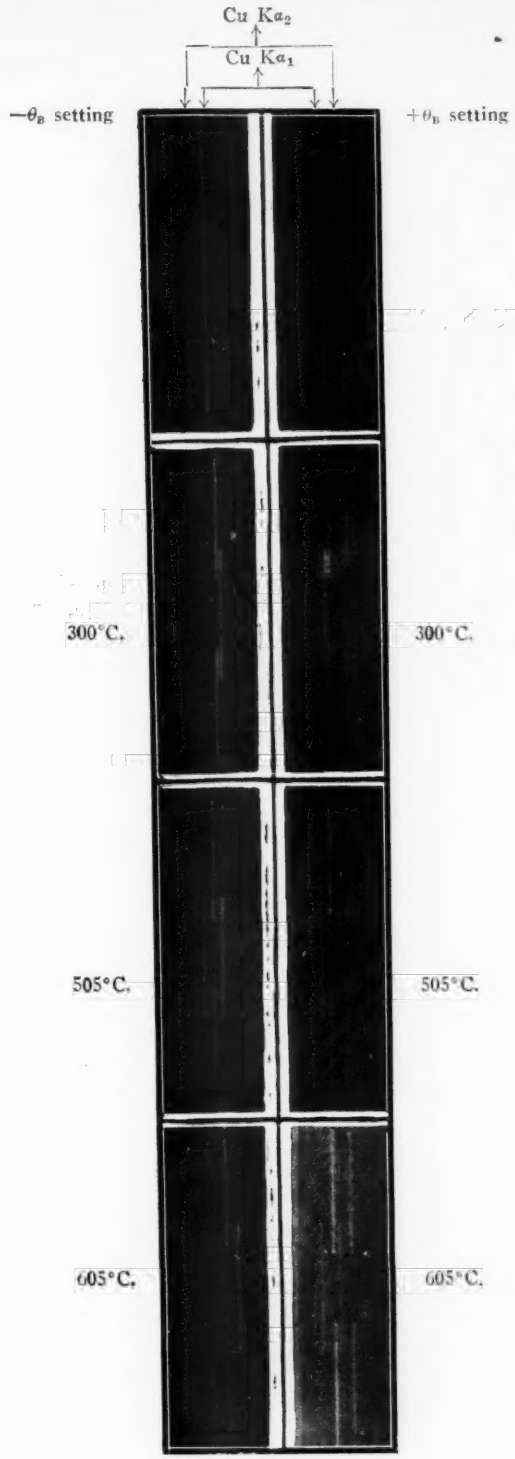

FIG. 6
Thermal Expansion of Diamond

TEMPERATURE VARIATIONS OF THE RAMAN FREQUENCIES IN DIAMOND

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1. Introduction

When the temperature of a crystal is raised the atoms get less tightly packed resulting in an increase in the inter-atomic distances and a corresponding diminution of the forces acting on them. The frequencies of atomic vibrations which are determined by the inter-atomic forces will therefore be decreased. These frequency changes should in turn be related to the expansion of the crystal. The actual form of the relationship will necessarily depend on the law of force between the atoms. For constructing a simple theory of thermal expansion, G. üneisen (1908) assumed that the relative change of any vibration frequency was directly proportional to the relative change in the volume. In other words,

$$-\frac{\Delta\nu_i}{\nu_i}\times\frac{V}{\Delta V}=-\frac{d(\log\nu_i)}{d(\log V)}=\gamma_i, \tag{1}$$

where γ_i is a constant. If we assume with Grüneisen (1912) that γ_i is the same for all the frequencies in the vibration spectrum of a crystal which is justified on the Debye theory, we then get from strictly thermodynamical considerations

$$-\frac{d(\log\nu)}{d(\log V)}=\gamma=\frac{\alpha V_0}{\chi_0 C_v}, \tag{2}$$

where γ is the well-known Grüneisen constant. V_0, χ_0 and C_v have the usual significance, namely volume, compressibility and specific heat of the crystal. Further, the quantity $\frac{d(\log\nu)}{d(\log V)}$ should be independent of temperature. These conclusions have an important bearing on the theory of the solid state. It is therefore necessary to see how far they are in agreement with facts in any particular case. No attempt appears to have been made to test the validity of the above conclusions in any particular case. The present investigation was therefore undertaken with a view to get reliable data on the thermal variation of the Raman frequencies in diamond, the thermal expansion of which has already been studied in detail by the author (Krishnan, 1946 *a*).

2. Previous Work

Ramaswamy (1930) who was the first to photograph the Raman spectrum of diamond investigated the effect of temperature on the principal Raman frequency (1332 cm.$^{-1}$) of diamond. He reported that the Raman line was not perceptibly shifted or decreased in intensity and sharpness when the diamond was heated up to 250° C. His negative result may be attributed either to the unsuitable way of heating the crystal or to the relatively small dispersion of the spectrograph employed by him. Robertson, Fox and Martin (1934) reported similar negative results on cooling the crystal to − 180° C.

Using the λ 4046 and λ 4358 excitation, Nayar (1941) measured the frequency shift of the principal line of diamond and its variation with temperature over the range of temperature from − 180° C. to 860° C. From the observed variation of the characteristic frequency, Nayar evaluated the thermal expansion coefficient of diamond and compared the same with the available data on thermal expansion which, however, covered only a short range of temperature. The experimental value was definitely higher than the theoretical value. Nayar's frequency-temperature curve in the region of high temperatures is not very reliable as it was based on observations made at three temperatures only in the range from 250° to 850° C.

3. Details of the Experiment

As is well known, the first order Raman spectrum of diamond exhibits only a single, sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ The other fundamental modes of oscillation of the diamond lattice are forbidden to appear in the first order spectrum. Some of them manifest themselves as octaves and combinations in the second order Raman spectrum (Krishnan, 1944 *a*, 1946 *b*). The temperature variations of the frequencies of the forbidden modes have therefore to be estimated from the observed thermal behaviour of the Raman lines appearing in the second order spectrum. As the second order lines are necessarily weak and not so sharp as the first order line (1332 cm.$^{-1}$), it is not possible to determine their temperature variations with the same degree of accuracy and over short ranges of temperature as could be attained in the case of the principal line at 1332 cm.$^{-1}$ Two independent sets of experiments had therefore to be carried out. In order to utilise the high resolving power of a quartz spectrograph in the ultra-violet and to take spectrum photographs with reasonably short exposures, the intense λ 2536·5 mercury resonance radiation was used for exciting the Raman spectrum. Diamonds of the ultra-violet transparent type were employed.

High Temperatures.—For work above room temperature a specially designed heater was constructed. It consisted of a thin rectangular steel tube ($4'' \times \frac{1}{2}'' \times \frac{1}{2}''$) provided with three circular holes ($\frac{1}{4}''$ in diameter) covered with quartz windows on three of its sides in the central portion of the tube. These served for illumination of the crystal supported inside the tube and for observation of the scattered light. The steel part of the heater was covered with a thin layer of mica and was closely wound over with nichrome wire set in a mixture of alumina and sodium silicate solution. To reduce losses due to radiation, an aluminium foil was stuck on to the outside of the furnace. Steady current was supplied to the heater from a set of accumulators. During an exposure the heater current was maintained at a constant value. The top of the furnace was closed by a disc to which was attached a thin metal tube. The tube supporting the furnace was clamped vertically to an adjustable stand.

The specimen of diamond which was in the form of a thin plate ($10 \times 6 \times 0{\cdot}6$ mm.) was fixed on the top of a silica rod $\frac{1}{4}''$ in diameter with its flat faces vertical and facing the most intense portion of a water-cooled magnet-controlled quartz arc. The light scattered through one of the straight edges of the diamond in the end—on position was focussed on the slit of the spectrograph. After the preliminary adjustments were made, the furnace was lowered into position. To determine the temperature of the diamond during exposures, a calibrated nichrome-constantan thermocouple was fixed permanently inside the furnace almost touching the diamond. Diamond being a good conductor of heat, its temperature was taken to be that of the air inside the furnace. At the highest temperature used, namely, 700° C., after switching on the current, it took about 20–30 minutes for the furnace to come to a steady state.

Low Temperatures.—For work below room temperature a demountable vacuum flask with an inner vessel of metal and an outer vessel of glass was employed. The lower end of the outer vessel was provided with two quartz windows. Through one of these windows the diamond was irradiated with the light from the mercury arc, while the observation of the scattered light was made through the second window. The thin plate of diamond was held in a copper block fixed to the bottom of the inner brass tube of the flask which formed the container for the refrigerant. The flanged joint between the inner and outer tubes at the top was sealed with Apiezon sealing compound, "Q". The flask was kept evacuated continuously with the aid of a Cenco Hyvac pump.

Principal Raman Frequency (1332 $cm.^{-1}$).—For measuring the temperature variation of the principal Raman line, a Hilger E1 quartz spectrograph

having a dispersion of about 44 cm.$^{-1}$/mm. in the λ 2625 region was used. With a slit-width of 0·01 mm., exposures of the order of two hours were required to get the line recorded with a reasonable intensity. With the furnace in position, the temperature of the diamond was 55° C. when no current was passed through the heater coil. With the low temperature apparatus, the temperature of the diamond was the same as that of the room temperature, *viz.*, 27° C., when no refrigerant was poured into the flask. It was therefore necessary to make accurate measurements of the frequency shift of the principal Raman line for these two temperatures. For each temperature a couple of photographs of the Raman spectrum was taken with an iron arc comparison spectrum partially overlapping the Raman spectrum. The plates were measured with a Hilger cross-slide micrometer reading up to 1/1000 mm. The mean values of the frequency shift at 27° and 55° were evaluated in the usual way.

Using a Hartmann diaphragm, two photographs of the Raman spectrum were recorded in juxtaposition on the same plate, one without any current passing through the heating coil, *i.e.*, the crystal being maintained at 55° C. and the other with the crystal heated to a known temperature. During the high temperature exposure, the furnace current was continuously regulated by hand in order to keep the temperature constant. It did not vary by more than 2° from the desired temperature.

The use of the high dispersion E1 spectrograph presented some difficulties in the beginning. Being of an all-metal type, it was susceptible to small variations of temperature. The spectrograph was housed in a separate double-walled cabin and the furnace, arc, etc., were placed outside. In between two exposures, the cabin door had to be opened for shifting the Hartmann diaphragm. While doing this, warm air from outside rushed into the cabin. Consequently the temperature of the spectrograph varied to such an extent as to produce a noticeable drift of the mercury lines in the spectrogram recorded subsequently. In order to minimise this trouble, the spectrograph was covered with two layers of woollen blankets which proved to be very effective. As a further check, the frequency change of the 1332 line was evaluated not from the observed shift of this line, but from the relative shift with reference to the nearest mercury lines on either side.

The frequency changes of the principal Raman line were determined for 13 different temperatures above 55° C., namely, 117°, 152°, 211°, 242°, 285°, 345°, 396°, 452°, 500°, 550°, 600°, 654° and 703° C. Two low temperature measurements were also obtained by using liquid air as refrigerant in one case and solid carbon dioxide-acetone mixture in the other case.

Second order Raman lines.—Using a Hilger E3 medium quartz spectrograph which had a dispersion of about 140 cm.$^{-1}$/mm., a heavily exposed Raman spectrum of diamond showing the second order lines was recorded with the specimen (N.C. 89) maintained at room temperature (30°) by fan cooling. Similar photographs were also taken on different plates with the crystal maintained successively at 390° C. and 620° C. The constant temperature furnace described earlier in the section was used for this purpose. The negatives were microphotometered, and from the microphotometric records the frequency shifts of the prominent second order lines were estimated.

4. Results

The frequencies of the principal Raman line at different temperatures are given in Table I and the variation with temperature is graphically represented by the curve in Fig. 1. The ordinates represent the decrease or

TABLE I

Frequencies of the principal Raman line in diamond at different temperatures

Temperature of	Frequency shift in cm.$^{-1}$
85	1333·2
195	1332·7
300	1331·8
328	1331·5
390	1330·4
425	1329·6
484	1327·7
515	1327·3
558	1327·0
618	1325·6
669	1324·4
725	1323·1
773	1322·2
823	1320·8
873	1318·9
927	1317·6
976	1316·0

increase in frequency shift from the value at 300° T. It will be noticed that the rate of decrease, *i.e.*, $-\frac{dv}{dT}$ is greater at higher temperatures. As the temperature is lowered the curve tends to flatten up. Comparing the results reported here with those of Nayar (1941), it is seen that although the general features of the ($\Delta\nu - T$) curve are similar in both cases, the actual values of the frequency shifts at higher temperatures are not in agreement. For example, when the temperature of the diamond was raised from room

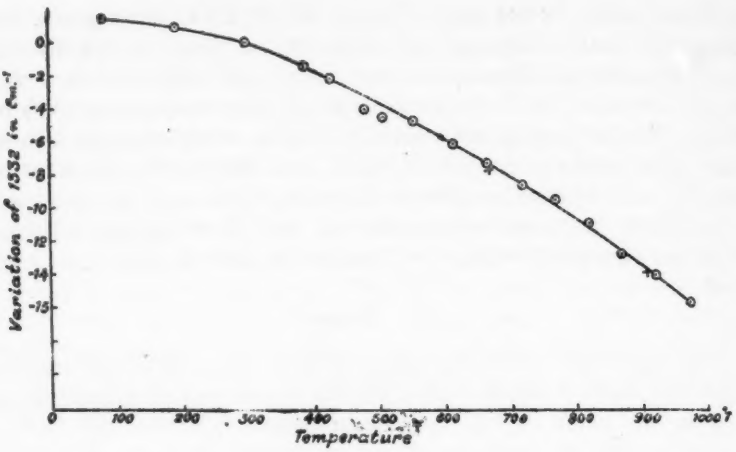

FIG. 1

FIG. 1. Frequency-Temperature curve for the principal Raman line of diamond

temperature to 632° C., Nayar recorded a change in the frequency equal to 10·2 wavenumbers. Actually, for the same range of temperature the author has observed a frequency change of 13·4 wavenumbers. The deviation increases with increasing temperature. In order to be sure that the observed deviation had nothing to do with the type of diamond used in the present investigation, the experiment was repeated for two temperatures using the same specimen of diamond with which the thermal expansion measurements were made (Krishnan, 1946 *a*) and which belonged to the ultraviolet opaque type. In an earlier publication (Krishnan, 1944) the author had shown that at room temperature there is no difference in the frequency shifts of the principal Raman line for the two types of diamond. Using the constant temperature furnace described in the previous section, a Hilger two prism spectrograph and λ 4358 excitation, the frequency changes for the ultraviolet opaque diamond were measured for two ranges of temperature, namely, 55°–398° C. and 55°–640° C. The values are plotted in Fig. 1. They are indicated by crosses and fall on the smooth curve, showing thereby that the temperature variations of the principal Raman frequency are the same for the two types of diamond in the range of temperature covered by the present investigation.

The smaller values for the frequency changes reported by Nayar (1941) may be attributed to the fact that in his experiments the thermo-couple might not have recorded the correct temperature of the diamond. As the specimen was kept at one end of the furnace, its temperature was in all

probability lower than the temperature inside the furnace. The thermo-couple which was supported inside the heater recorded the correct temperature of the latter and not of the crystal. In the present experiment the diamond which was only 1 cm. in length was supported inside the furnace which was about 4″ long. In order to eliminate air currents passing through the furnace, the top was completely closed by a metal disc, while the bottom was partially covered by the supporting quartz rod. The calibration curve for the thermo-couple was checked against the readings taken with a standard thermometer.

Table II gives the values of the frequency shifts of some of the prominent second order Raman lines at three different temperatures. It is evident from the figures given in Table II that for the same increase of temperature, the proportional change in the frequency shift is different for different second order Raman lines.

TABLE II

Frequency shifts in wavenumbers of the prominent second order Raman lines in Diamond

30°	390°	620°
2666	2652	2640
2502	2494	2486
2460	2449	2438
2176	2171	2158

5. Discussion of Results

The quantity $\frac{d(\log \nu)}{d(\log V)}$ can be written in the form:—

$$\frac{d(\log \nu)}{d(\log V)} = \frac{d\nu}{\nu} \cdot \frac{V}{dV} = \frac{\Delta \nu}{\nu} \cdot \frac{1}{\bar{\alpha}(T_2 - T_1)}, \qquad (3)$$

where $\Delta \nu$ is the diminution in frequency ν in the temperature range T_1 to T_2 and $\bar{\alpha}$ is the mean coefficient of thermal expansion over the same range. In column 3 of Table III are given the observed values of the mean coefficient of thermal (volume) expansion for the different temperature ranges entered in column 1. The values below the horizontal line are those reported by the author (Krishnan, 1946 *a*), while those above the horizontal line were taken from Röntgen's (1912) measurements. The corresponding values of $\Delta \nu$ in wavenumbers for the principal Raman line (1332 cm.$^{-1}$) in diamond are read off from the curve reproduced in Fig. 1 and are given in column 4.

The quantity $\gamma_{1332}\left\{=\frac{d(\log \nu)}{d(\log V)}\right\}$ has been evaluated using equation (3). The values for the different temperature ranges are entered in column 5 of Table III.

TABLE III

Temperature range ° T	Mean Temperature ° T.	$\bar{\alpha} \times 10^6$	$\Delta\nu_{1332}$ in cm.$^{-1}$	γ_{1332}	$\gamma = \frac{\alpha V_0}{\chi_0 C_v}$
84·8–194·1	139·5	0·54	0·5	6·4	1·19
194·1–273·2	233·6	1·74	0·6	3·3	1·03
273·2–296·2	284·7	2·91	0·3	3·4	1·10
296·2–351·1	323	3·87	0·9	3·2	1·15
301–378	339·5	4·36	1·3	2·9	1·20
378–478	428	6·51	1·9	2·7	1·27
478–573	525	8·52	2·0	1·9	1·31
573–678	625	9·84	2·45	1·8	1·3
678–778	728	10·86	2·5	1·7	1·3
778–878	828	11·76	2·7	1·7	1·3

The last column in the above table gives the values of the Grüneisen number $\gamma\left(=\frac{\alpha V_0}{\chi_0 C_v}\right)$ taken from another paper by the author (Krishnan, 1946*a*) appearing in this symposium. It is evident that γ_{1332} far from being a constant, *decreases* steadily from a value of 6·4 at 85° T. to about 1·8 at 600° T. Above 600° T. its value remains constant. The temperature dependence of γ_{1332} is graphically represented in Fig. 2. The portion of the curve below

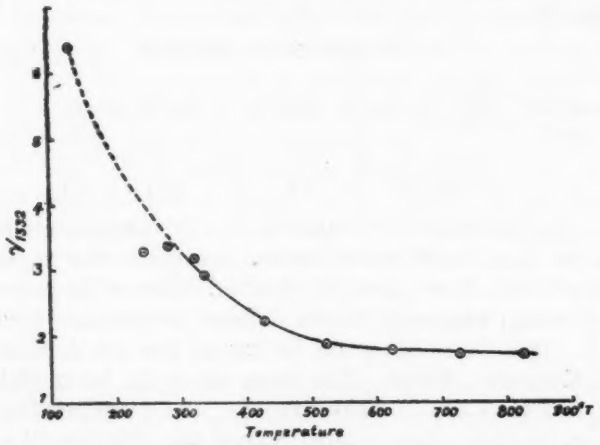

FIG. 2. Temperature dependence of γ_{1332}, *i.e.*, the ratio of the relative change of frequency to the relative change of volume

273° T. is shown by a broken line as the values of γ_{1332} are not so accurate as those at high temperatures owing to the small values of $\bar{\alpha}$ and $\Delta\nu$. Comparing the values given in columns 5 and 6 in Table III one finds that throughout the range of temperature investigated here γ_{1332} is not equal to the Grüneisen number γ.

The mean values of γ_i for the prominent second order Raman lines for the temperature ranges 30–390° C. and 30–620° C. have been evaluated from the observed displacements of the lines. The results are entered in Table IV. As is to be expected, γ_i is the same for the 1332 line and its octave at 2666 cm.$^{-1}$ Different frequencies have in fact different γ_i's, that for the principal Raman line (1332 cm.$^{-1}$) being the highest. It is interesting to

TABLE IV

Raman line	$\bar{\gamma}_i$	$\bar{\gamma}_i$
	30–390°	30°–620°
1332	2·0	1·9
2666	2·0	1·9
2502	1·2	1·2
2460	1·7	1·7
2176	0·8	1·6

note that γ_i for the line 2176 increases with temperature. This line is evidently the octave of the prominent lattice line with a frequency shift of 1088 cm.$^{-1}$ appearing in the luminescence and absorption spectra of diamond.

Curves showing the relation between the increase of lattice spacing with increase of temperature and the corresponding decrease of frequency have been reproduced in Fig. 3 for the Raman lines 1332, 2502, 2460 and 2176 cm.$^{-1}$ The data on the lattice spacing variation were taken from the author's paper on the thermal expansion of diamond. Above room temperature, *i.e.*, 300° T. the relationship is nearly linear for the lines 1332, 2460 and 2502 cm.$^{-1}$, but with different slopes. The variation of the frequency of the 2176 line is represented by a more complicated curve. The relative decrease in frequency shift of this line is smaller at low temperatures, and increases rapidly above 400° C. The difference in the thermal behaviour of the Raman lines is due to the fact that the inter-atomic forces inside the diamond lattice are affected by temperature to varying extent. On the basis of the lattice lines observed in luminescence, the Raman lines 2502 cm.$^{-1}$ and 2176 cm.$^{-1}$ can be assigned as the octaves of the fundamentals with frequency shifts 1251

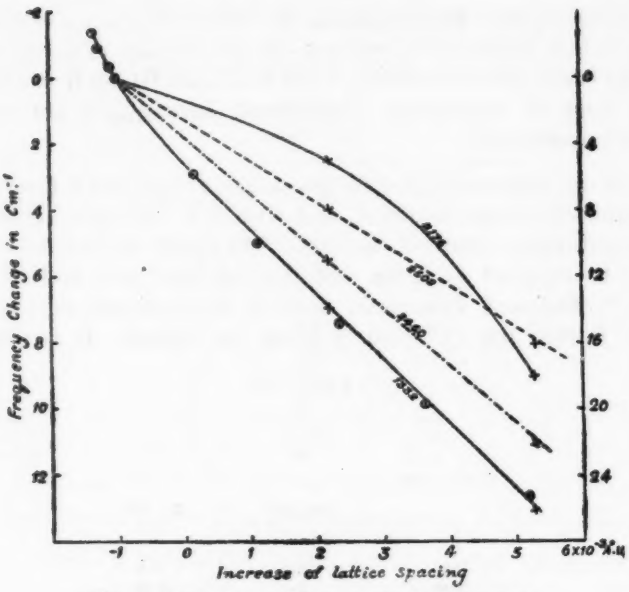

FIG. 3. Dependence of frequency on lattice spacing

and 1088 cm.$^{-1}$ The lattice lines with frequency shifts 1332, 1251 and 1088 correspond to the modes F_2, H_4 and K_3 as designated by Bhagavantam (1943). The expressions for the frequencies are given in Table V.

TABLE V

Mode	$4\pi^2\nu^2$	Observed ν in cm.$^{-1}$
F_2 ..	$\frac{8K \times 64K_\alpha}{3m}$	1332
H_4 ..	$\frac{8K \times 4K_\alpha + 12K''}{3m}$	1251
K_3 ..	$\frac{6K + 24K''}{3m}$	1088

K, K_α and K″ are the respective force constants arising from the primary valence bond, the directed valence bond and the repulsion between the next nearest neighbours. Their values are according to Dayal (1944):—

$K = 0{\cdot}314 \times 10^6$ dynes/cm.

$K'' = 0{\cdot}039 \times 10^6$,,

$K_\alpha = 0{\cdot}0197 \times 10^6$,,

From the observed variations of the frequencies of F_2, H_4 and K_3 with lattice spacing the corresponding changes in the force constants have been estimated. When the temperature of the diamond is raised from 300° T. to 800° T. the values of K and K_α *decrease* by $3{\cdot}7 \times 10^3$ dynes/cm. and $2{\cdot}5 \times 10^3$ dynes/cm. respectively, whereas the value of K″ increases by $3{\cdot}4 \times 10^2$ dynes/cm. The decrease in the value of K is of the same order of magnitude, but definitely greater than that of the force constant of the C—C bond with increase in the equilibrium nuclear distance as deduced from band spectrum data.

6. Width of the 1332 Line and its Interpretation

The author had remarked in one of the earlier papers (Krishnan, 1944 *b*) that the principal Raman line in diamond, though sharp, had a finite width at room temperature. As the temperature is raised, this line is found to broaden, the aggregate intensity of the line being greater at the higher temperature. The widths of the line at different temperatures have been estimated from the microphotometric records of the corresponding spectrograms. Typical microphotometric curves showing the variation of line width with

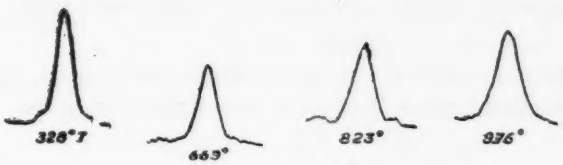

Fig. 4. Microphotometric records of the 1332 line at different temperatures

temperature are reproduced in Fig. 4. The relation between the half width of the 1332 line at half intensity and the temperature of the diamond is illustrated by the curve reproduced in Fig. 5. The values entered as ordinates are the measured half widths without making any allowance for the finite

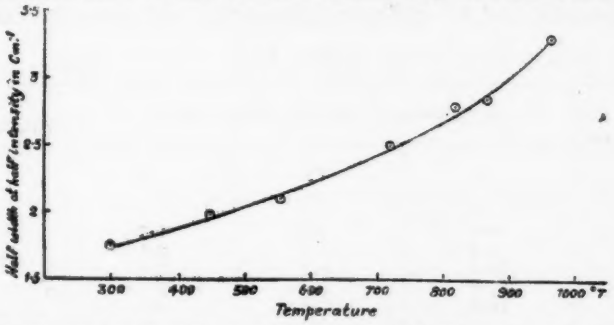

Fig. 5. Temperature dependence of the half width at half intensity of the 1332 line

width of the slit and other factors connected with the spectrograph. A mercury line which was recorded on the plate with roughly the same intensity as the Raman line had a half width at half intensity of 1·5 wavenumbers. The rate of increase of the breadth of the 1332 line increases with temperature. The enhanced width of the 1332 line at high temperatures cannot be attributed to temperature variations of the furnace as the latter never exceeded 2° either way.

The finite width of the Raman line at any particular temperature may be attributed to the thermal fluctuations in density inside the crystal. On the basis of the new lattice dynamics, if the atoms within an element of volume in the crystal of sufficient extension are arranged with perfect regularity in the lattice, their vibrations would be strictly monochromatic. But due to thermal agitation the lattice spacings undergo fluctuations. As the domain gets compressed, the atomic vibration frequency increases and when it expands, the frequency gets diminished. As the compressions and expansions are of varying magnitude, the frequency will vary continuously about the mean value, giving rise to a finite width for the Raman line. The mean square of the fluctuations in volume is given by the well-known formula

$$\overline{(\Delta V)^2} = kT\chi V \tag{4}$$

where k is the gas constant, χ compressibility and V is the volume of the domain. The relative mean fluctuation in volume is given by

$$\frac{\sqrt{\overline{(\Delta V)^2}}}{V} = \sqrt{\frac{kT\chi}{V}}. \tag{5}$$

From the observed variations of the frequency shift of the 1332 line with increase in lattice spacing, the half width of the line arising from the relative mean fluctuation in a volume element at any desired temperature can be evaluated. The values of the half width for three different sizes of the volume element, namely, $V_1 = 8$ times, $V_2 = 64$ times and $V_3 = 512$ times the volume of the unit cube, and for different temperatures are given in Table VI.

TABLE VI

Temperature °T.	Calculated mean half width in cm.$^{-1}$			Observed value of half width*
	V_1	F_2	V_3	
300	10·8	4·3	1·7	1·7
500	13·7	5·1	2·1	2·1
700	16·4	6·1	2·5	2·4
900	18·0	6·9	2·8	2·9
970	18·8	7·1	2·9	3·6

* No correction has been made for the width arising from the finite width of the exciting line, width of slit used and other factors connected with the spectrograph.

Comparing the figures given in Table VI, it is evident that for a volume element which has 8 times the linear dimensions of the unit cubic cell, the calculated half width of the 1332 line is of the same order of magnitude as the observed half width at half intensity.

In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman for useful discussions during the progress of these investigations.

Summary

With a high dispersion spectrograph, a diamond of the ultraviolet transparent type and the mercury λ 2536·5 excitation, the principal Raman frequency has been measured and is found to decrease from 1333·2 cm.$^{-1}$ at 85° T. to 1316·0 cm.$^{-1}$ at 975° T. Identical results are obtained with a diamond of the ultraviolet opaque type and the λ 4358 excitation. The temperature dependence of the more prominent second order Raman frequencies has also been investigated. The relative change of the principal frequency with relative change of volume decreases from a high value at 85° T. to a constant small value above 500° T. and differs greatly from the so-called Grüneisen constant. The different lattice and superlattice frequencies behave differently in respect of their temperature variation and this has been explained as due to differences in the rate of change with temperature of the different force constants which determine the vibration frequencies of the diamond lattice.

The 1332 line has a finite width which increases with temperature. This may be explained as due to the changes of lattice frequency arising from the thermal fluctuations of density in the volume elements of the crystal, if the effective linear dimensions of a volume element are assumed to be about 8 times as large as the edge of the unit cubic cell.

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ON THE CRYSTAL SYMMETRY OF DIAMOND AND ITS X-RAY REFLECTIONS

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§1. On the basis of the observed crystal forms of diamond, especially of grooved octahedra, duplex tetrahedra and such other typical twin forms, the earlier crystallographers assigned diamond to the hemimorphic hemihedral or the tetrahedral (Td) class of the cubic system (*vide* Groth, 1895; Liebisch, 1896; Miers, 1902; Hintze, 1904). That this is the case in the majority of diamonds is confirmed by observations of the infra-red absorption of diamond by a number of investigators (Ångstrom, 1892; Julius, 1893; Reinkober, 1911) and particularly by Robertson, Fox and Martin (1934), who found that a majority of diamonds exhibit a strong infra-red absorption in the region of 8μ, while in other diamonds, the absorption is absent. Applying the well-known selection rules for infra-red absorption (Placzek, 1934), it becomes obvious that the former class of diamonds should possess only tetrahedral (Td) symmetry, while the latter should possess the full octahedral (Oh) symmetry of the cubic system (Raman, 1944). An alternative explanation that the infra-red absorption arises from the presence of impurities or of structural imperfections is ruled out by the fact that the diamonds that show the absorption most prominently are precisely those that possess the maximum amount of crystal perfection (Ramachandran, 1944 *b*), while *per contra* diamonds that possess a large mosaic structure are transparent to the infra-red (Hariharan, 1944; Ramachandran, 1944 *a*). To explain these facts regarding infra-red absorption as well as a whole series of other phenomena exhibited by diamond, Sir C. V. Raman (1944) put forward considerations which indicate that there are four possible structures for diamond, two with tetrahedral symmetry and two others with octahedral symmetry, and in doing so remarked that the data regarding the X-ray reflections given by diamond are consistent with the existence of these four forms. In the present paper, this question is considered in a formal and rigorous manner. The consequences of the difference in symmetry of the various structures

are worked out, and are compared with the observed X-ray behaviour of diamond.*

We shall accept the results of X-ray analysis that the diamond structure consists of two interpenetrating face-centred cubic lattices, with the carbon atoms in the basis occupying the positions 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. It may be pointed out that the main facts which led to this structure were the absence of the 200 and the 222 X-ray reflections observed by the earliest investigators (Bragg and Bragg, 1913). We shall accept the structure described above, since it fits in well with the quadrivalence of carbon, a well-known chemical result. The questions to be decided are: (*a*) what the symmetry of the electronic configurations of the individual carbon atoms is, and (*b*) what the relationship between the electronic structures of the two carbon atoms is. In this connection, we have also to discuss the results of later experimenters, who have remarked that the 222 reflection is present feebly, *e.g.*, Bragg, 1921; Ehrenberg, Ewald and Mark, 1928.

§2. On account of the special positions which the carbon atoms occupy in the space-lattice, they should possess a symmetry not lower than that of the point-group Td. For the purpose of the following discussion, we shall take it that they possess that symmetry. This means that if $\rho_1(xyz)$ is the electronic charge density at the point xyz, then it is the same at the following 24 equivalent points:

$$\begin{array}{llllll} xyz\,; & zxy\,; & yzx\,; & yxz\,; & zyx\,; & xzy\,; \\ x\bar{y}\bar{z}\,; & z\bar{x}\bar{y}\,; & y\bar{z}\bar{x}\,; & y\bar{x}\bar{z}\,; & z\bar{y}\bar{x}\,; & x\bar{z}\bar{y}\,; \\ \bar{x}y\bar{z}\,; & \bar{z}x\bar{y}\,; & \bar{y}z\bar{x}\,; & \bar{y}x\bar{z}\,; & \bar{z}y\bar{x}\,; & \bar{x}z\bar{y}\,; \\ \bar{x}\bar{y}z\,; & \bar{z}\bar{x}y\,; & \bar{y}\bar{z}x\,; & \bar{y}\bar{x}z\,; & \bar{z}\bar{y}x\,; & \bar{x}\bar{z}y\,; \end{array} \qquad (1)$$

This set may be represented by the symbol $\{xyz\}$. Similarly, the electronic charge densities at the points $\frac{1}{4}\frac{1}{4}\frac{1}{4}+\{xyz\}$ are all equal, which may be denoted by $\rho_2(xyz)$. Note that no assumption is made as to the relationship between ρ_1 and ρ_2. For the present, it is supposed that the two carbon atoms are different. It is also to be noted that $\rho(xyz)$ is not necessarily equal to $\rho(\bar{x}\bar{y}\bar{z})$.

We shall now derive an expression for the structure factor for the *hkl* reflection with such a structure. Consider a set of 96 volume elements, each of magnitude dv, surrounding the points $\{xyz\}$, $\{\bar{x}\bar{y}\bar{z}\}$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}+\{xyz\}$

* A preliminary report by the author (1945) appeared in *Nature*, in which some specific points raised by Mrs. Lonsdale (1945) regarding the X-ray behaviour of the various forms of diamond were answered.

and $\frac{1}{2}\frac{1}{2}\frac{1}{2} + (\bar{x}\bar{y}\bar{z})$. Denoting by $\phi(hkl)$ the structure factor corresponding to these volume elements, it can be shown that

$$\phi(hkl) = \{\rho_1(xyz)(A + iB) + \rho_1(\bar{x}\bar{y}\bar{z})(A - iB) + \rho_2(xyz)(A + iB).$$
$$\exp 2\pi i(h + k + l)/4 + \rho_2(\bar{x}\bar{y}\bar{z})(A - iB)\exp 2\pi i(h + k + l)/4\}\, dv, \quad (2)$$

where
$$A = 16\cos 2\pi\frac{h-k}{4}\cos 2\pi\frac{k-l}{4}\cos 2\pi\frac{l-h}{4}.$$
$$\{\cos 2\pi lz(\cos 2\pi hx\cos 2\pi ky + \cos 2\pi kx\cos 2\pi hy)$$
$$+ \cos 2\pi hz(\cos 2\pi kx\cos 2\pi ly + \cos 2\pi lx\cos 2\pi ky)$$
$$+ \cos 2\pi kz(\cos 2\pi lx\cos 2\pi hy + \cos 2\pi hx\cos 2\pi ly)\} \quad (3)$$

and
$$B = -16\cos 2\pi\frac{h-k}{4}\cos 2\pi\frac{k-l}{4}\cos 2\pi\frac{l-h}{4}$$
$$\{\sin 2\pi lz(\sin 2\pi hx\sin 2\pi ky + \sin 2\pi kx\sin 2\pi hy)$$
$$+ \sin 2\pi hz(\sin 2\pi kx\sin 2\pi ly + \sin 2\pi lx\sin 2\pi ky)$$
$$+ \sin 2\pi kz(\sin 2\pi lx\sin 2\pi hy + \sin 2\pi hx\sin 2\pi ly)\}. \quad (4)$$

The crystal structure factor $F(hkl)$ can be obtained by integrating $\phi(hkl)$ over the appropriate volume. From the above expressions, the elementary structure factors corresponding to the 200 and the 222 reflections are:

$$\phi(200) = Adv\{\rho_1(xyz) + \rho_1(\bar{x}\bar{y}\bar{z}) - \rho_2(xyz) - \rho_2(\bar{x}\bar{y}\bar{z})\} \quad (5)$$

$$\phi(222) = iBdv\{\rho_1(xyz) - \rho_1(\bar{x}\bar{y}\bar{z}) - \rho_2(xyz) + \rho_2(\bar{x}\bar{y}\bar{z})\} \quad (6)$$

Consequently, the condition that the 200 or the 222 reflection should vanish is that the quantity within the double brackets in Eq. (5) or (6) respectively should be equal to zero.

Let us now consider the circumstances under which the structure possesses octahedral symmetry. This can occur in one of two possible ways: the individual carbon atoms can themselves possess octahedral symmetry, or the two carbon atoms can be tetrahedral, but possess identical configurations with the two tetrahedral atoms pointing in opposite directions. In the latter case, the structure has a centre of symmetry at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, and belongs to the space group O_h^7. The two conditions can algebraically be represented as follows:

$$\left.\begin{array}{ll} (a) & \rho_1(xyz) = \rho_1(\bar{x}\bar{y}\bar{z});\quad \rho_2(xyz) = \rho_2(\bar{x}\bar{y}\bar{z}) \\ (b) & \rho_1(xyz) = \rho_2(\bar{x}\bar{y}\bar{z});\quad \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(xyz) \end{array}\right\} \quad (7)$$

A careful comparison of the conditions for the vanishing of the 200 and the 222 reflections with those for the existence of octahedral symmetry shows that there is really no interrelation between them, though if 7 (*b*) subsists, the 200 reflection automatically vanishes. In other words, from the knowledge that the 200 or the 222 reflection is present or absent, one cannot uniquely conclude that the crystal has tetrahedral or octahedral symmetry and *vice versa*.

§3. It is a fairly well-established experimental fact that the 200 reflection does not appear with diamond. Taking this into consideration, let us consider what restrictions it imposes on the structure. From (5), the condition that 200 should vanish is

$$\rho_1(xyz) + \rho_1(\bar{x}\bar{y}z) = \rho_2(xyz) + \rho_2(\bar{x}\bar{y}z), \tag{8}$$

i.e., if we take two points in each of the atoms such that they are equidistant in opposite directions from the centre of the atoms, then the sum of the electronic charge densities at these two points should be the same for both the atoms. From this, it follows that the total charge in spherical shells surrounding the two atoms are equal, provided the radii of the two shells is the same, independent of the magnitude of the radius. This explains why diamond is not a polar substance, and also makes it comprehensible why diamond does not exhibit any appreciable piezo- or pyro-electric properties. However, the condition (8) does not impose any restriction at all on the symmetry of the structure.

We shall now consider the various structures that are possible, subject to the condition (8). In this connection, it will be convenient to use a special nomenclature. It will be seen that if

$$\rho_1(xyz) = \rho_2(\bar{x}\bar{y}z) \text{ and } \rho_1(\bar{x}\bar{y}z) = \rho_2(xyz),$$

then the equation (8) is satisfied. This is identical with (7 *b*), and the structure has a centre of symmetry mid-way between the two atoms. We shall therefore designate it as a symmetric structure. On the other hand, we shall call a structure antisymmetric if

$$\rho_1(xyz) = \rho_2(xyz) \text{ and } \rho_1(\bar{x}\bar{y}z) = \rho_2(\bar{x}\bar{y}z). \tag{9}$$

It is obvious that this also satisfies Eq. (8). It is easy to show that the ρ's in Eq. (8) can always be split into a symmetric and an antisymmetric component, and that the manner in which this can be done is unique if the ρ's are known quantities. For let

$$\rho_1(xyz) = \alpha + \beta \quad \text{and } \rho_1(\bar{x}\bar{y}z) = \alpha' + \beta'. \tag{10}$$

where α and β are respectively the symmetric and the antisymmetric components. Then, by the definitions above,

$$\rho_2(xyz) = \alpha' + \beta \qquad \text{and } \rho_2(\bar{x}\bar{y}\bar{z}) = \alpha + \beta'. \tag{11}$$

The four equations in (10) and (11) form a set of linear equations in the four unknown α, β, α', β' and can therefore be uniquely solved. If, on the other hand, it is only known that the 200 reflection is absent, then all that can be said about the electronic distribution is that it consists of a symmetric component α and an antisymmetric component β, the ratio of α to β being undetermined.

Now, it is evident that if $\beta = \beta' = 0$, *i.e.*, if the antisymmetric component is entirely absent, then the structure possesses octahedral symmetry. But if the β's are finite, however small they might be, then the structure has only tetrahedral symmetry. Since various physical properties of the tetrahedral and octahedral modifications of diamond do not differ notably (as, for example, the lattice spacing, the principal vibrational frequency of 1332 cm.$^{-1}$, etc.), the differences in the electronic configurations must be small. In other words, the tetrahedral symmetry must arise from the presence of a relatively small proportion of an antisymmetric distribution. This would explain why the infra-red absorption observed in tetrahedral diamond is not very strong, a thickness of 1 mm. producing only about 90% absorption (Ramanathan, 1946) in comparison with the practically cent. per cent. absorption of the alkali halides in extremely small thickness of the order of a few microns (Barnes, 1932).

§4. We shall now consider the various possibilities for the 222 reflection, *subject to the condition that the* 200 *reflection vanishes.* From (6), 222 vanishes if

$$\rho_1(xyz) - \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(xyz) - \rho_2(\bar{x}\bar{y}\bar{z}). \tag{12}$$

Combining (12) with (8), the conditions that the 200 and the 222 reflections should simultaneously vanish can be put in the form

$$\rho_1(xyz) = \rho_2(xyz); \quad \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(\bar{x}\bar{y}\bar{z}).$$

These are identical with (9), which means that 222 is absent if and only if the structure is completely antisymmetric. On the other hand, a symmetric distribution must necessarily give rise to a finite 222 structure amplitude. These statements however need a qualification. In the special case, in which the individual carbon atoms possess octahedral symmetry, the distinction between the terms symmetric and antisymmetric disappears, since the electronic charge distribution satisfies the conditions for both. The 222 reflection would be absent for this structure.

We are now in a position to discuss the origin of the observed feeble 222 reflection referred to in §1. If we assume that this is a genuine Bragg reflection, then the octahedral diamond should have an electronic distribution of the symmetric type with no antisymmetric component whatsoever. The tetrahedral modification must arise from the presence of a small proportion of an antisymmetric distribution as mentioned in §3. It can be shown that the structure amplitudes for reflections like 400 and 220 for which $h + k + l = 4n$ will be unaffected, while that for 222 will theoretically be different, the difference however being small, since it is proportional to the ratio of the antisymmetric to the symmetric component.

Pisharoty (1941) has suggested that the 222 reflection is purely a modified or quantum reflection. If this is the case, then, in the octahedral diamond, each of the carbon atoms should possess octahedral symmetry. Here also, the tetrahedral modification must arise from the presence of a small proportion of the antisymmetric distribution. The 222 reflection is absent for both, and reflections hkl with $h + k + l = 4n$ are also unaffected.

My sincere thanks are due to Prof. Sir C. V. Raman for the many illuminating discussions I had with him during the preparation of this paper.

Summary

The problem of the symmetry of the diamond structure in relation to its X-ray behaviour is considered in a formal manner. It is shown that the presence or absence of the 200 or the 222 reflection cannot uniquely decide whether the symmetry is tetrahedral or octahedral. The 200 reflection is shown to be absent if the structure is either completely symmetric or antisymmetric with respect to the centre of inversion at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ or if the two distributions are superposed in any arbitrary ratio. The 222 reflection is, however, absent only in the fully antisymmetric case. Making use of these results, the nature of the structures that are possible for the tetrahedral and the octahedral modifications of diamond are discussed.

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ON THE NATURE AND ORIGIN OF THE LAMINATIONS OBSERVED IN DIAMOND

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1. Introduction

During their investigations on the birefringence exhibited by both crystals and cleavage plates of diamond, Raman and Rendall (1944) found that, quite apart from the irregular patches of restoration of light seen under crossed polaroids, many diamonds exhibit a " geometric pattern " consisting of bright streaks running in various directions. They also found that the axes of birefringence of these coincided with the direction of the streaks and the direction perpendicular to them. As a result of their studies, they came to the conclusion that the geometric birefringence is a photo-elastic effect occurring as a result of the juxtaposition of layers of diamond whose lattice spacing is slightly different from the rest of the crystal surrounding it. The present paper mainly deals with more detailed investigations carried out by the author regarding these phenomena. The studies were confined to cleavage plates of diamond, of which numerous examples were available in the personal collection of Sir C. V. Raman.

In the experiments of Raman and Rendall, fine streaks and lines were found in only a few cases; in many others only broad bands running nearly parallel to one another were seen. These differences must be attributed to an inherent defect in the method of observation that was employed, namely that the cleavage plates were always viewed normally. For, supposing that the intruding layers are not normal to the surface, but are inclined to it, then when viewed normally they would overlap one another and mutually obscure the details. In favourable cases, in which the laminæ are not too fine and are small in number, the overlapping may not completely obliterate them, and they may still be observable. But generally the details in the pattern will be washed out. It is obvious that the proper method of observation is to view them in such a position that the light traverses the crystal parallel to the laminæ. In the present investigation, this was achieved by using the Federov universal rotation apparatus in conjunction with a petrographic

microscope. In addition, quantitative data regarding the sign and magnitude of the birefringence have been obtained by the use of a Babinet compensator, together with the above apparatus. These studies have brought out new facts and have helped in understanding the nature and origin of the laminations.

2. Experimental Procedure in General

The present investigation can be divided into two parts: (*a*) a detailed study of the birefringence exhibited by diamond with special reference to the orientation of the laminæ and of the axes of birefringence, and (*b*) a study of the magnitude of the birefringence and of the nature of the stresses that give rise to this.

The experiments were all carried out with a Winkel-Zeiss petrological research microscope, model VI M, which had a large range of adjustments and had facilities for the use of a Federov universal stage and a Babinet compensator in conjunction with it. On account of the fact that the birefringence phenomena were observed with a microscope which has a relatively small field of view, only sensibly parallel plates of diamond could be studied. With wedge-shaped diamonds in which the two surfaces were appreciably inclined to each other, the incident light was refracted away so that it did not enter the microscope at all.

The Federov stage was a large one capable of rotation about four axes, and was mounted on the rotating stage of the microscope. The specimen of diamond was placed on the central glass disc of the Federov stage, with or without the pair of hemispherical glass segments. For rapid comparison of different diamonds, and for studies where the crystal was not inclined very much, the glass segments were dispensed with. The segments with a suitable immersion liquid were, however, useful in studying phenomena which could not be observed without them. The spherical glass segments used had a refractive index $\mu = 1{\cdot}649$ (the maximum that was available) and α-monobromonaphthalene with $\mu = 1{\cdot}65$ was used as the immersion fluid.

The microscope was invariably used at a small magnification, the objective having a magnification 2·5 and the eye-piece 6, 9 or 12 as was found convenient. With the glass spheres, a special achromatic objective having a magnification 7 was sometimes used, with the same eye-pieces as before.

The Babinet compensator was in a form in which it could be mounted on the microscope in place of the eye-piece. Measurements with this could be taken either visually using the micrometer screw of the instrument, or photographically. Either method was used, as was found convenient,

A large number of visual observations were made with a variety of specimens of diamond. Many of these were photographed. A Microdak photographic equipment supplied by Eastman Kodak Co., was used for this purpose. A selection of these photographs representing the main results of the investigation is reproduced in the plates accompanying the paper. The magnification in each case is given in the legends describing the photographs.

3. Studies on the Geometric Characters of the Birefringence

As already remarked, observations of Raman and Rendall on the birefringence patterns of diamonds have brought to light the existence of 'geometric' birefringence in which lines or parallel striations are seen running at 60° or 90°. It is therefore natural to suppose that these striations must be associated with the crystallographic planes of the crystal. For instance, with plates of octahedral cleavage (most of the plates studied had this cleavage), the three other sets of octahedral planes intersect the surface along lines which run at angles of 60° to one another. That the streaks in the birefringence pattern actually arise in this manner was recognised early in the course of the present investigation by determining the orientation of the crystal plate by means of X-rays. It was then found that the directions of the lines in birefringence are invariably parallel to the intersections of one or more octahedral (111) planes with the surface of the diamond. In less common cases, they were parallel to the intersections of some of the dodecahedral (110) planes with the surface.

An interesting point arises in this connection. Let us consider the intersections of the various octahedral and dodecahedral planes with the (111) plane. These would be as shown in Fig. 1. Of these, the three directions *a a'*, *b b'*, and *c c'*, are those along each of which one octahedral and one dodecahedral plane intersects the surface, *e.g.* $[01\bar{1}]$ is the intersection of the $(\bar{1}11)$ and the (011) planes with the surface (111) plane. However, A A', B B' and C C' can represent only the intersections of dodecahedral planes, these having the indices $(01\bar{1})$, $(10\bar{1})$ and $(1\bar{1}0)$ respectively. One thus sees that a knowledge of the azimuth α of the intersection (*viz.*, the angle made by the line with a reference line on the surface) alone is not sufficient to fix the orientation of the laminations completely. It is also necessary to know the inclination i of the laminæ to the normal to the surface. For dodecahedral planes intersecting along OA, OB and OC this angle is 0°, while for the other dodecahedral planes it is 35° 16'. For all the octahedral planes, the inclination is 19° 28'.

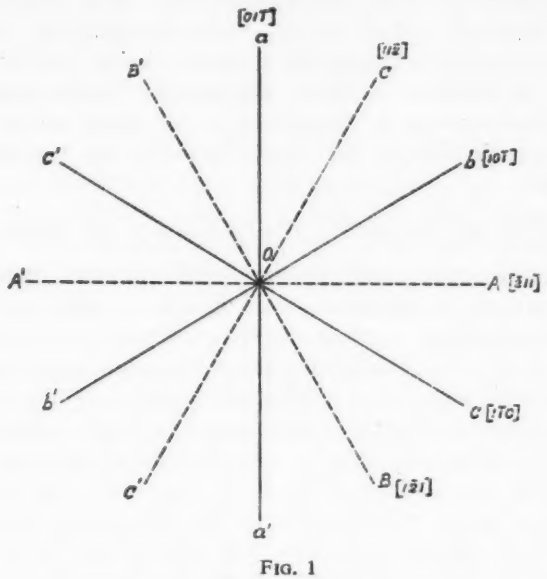

FIG. 1

The determination of the azimuth and inclination is most accurately done by using the Federov stage. The diamond was placed on the central glass plate of the Federov stage, and the birefringence pattern between crossed nicols was observed by means of the polarising microscope under low magnification. The Federov stage was adjusted so that the principal horizontal axis was parallel to one of the cross-wires of the microscope. The axis of rotation of the tilting stage was also made parallel to the principal horizontal axis. Keeping the tilting stage horizontal, the inner glass disc on which the diamond was placed was rotated in such a way that the birefringence streak (or set of lines as the case may be) was parallel to the cross-wire of the microscope to which the axes of the Federov stage were parallel. (Hereafter, by the term cross-wire of the microscope, we shall always mean this cross-wire). The crossed nicols were also rotated together until the required set of lines in the birefringence pattern were seen most clearly. Now on inclining the stage, it was found that the birefringence pattern either sharpened up or became more diffuse. If the latter happened, the stage was rotated in the opposite direction, when it sharpened up. It was generally found that the lines were sharpest at a certain angle, beyond which they became more and more diffuse.

The reason for the sharpening at certain inclinations is obviously that the laminations which give rise to the birefringence are oriented in a particular direction. When the light passes parallel to these laminæ, the pattern is sharp and well resolved. On the other hand, if the crystal is tilted away from this position, then the light traverses across a few of the laminæ, and the pattern overlaps portions of itself, thus becoming confused. Hence, the position at which the birefringence pattern is clearest and most well-defined is that at which the light passes parallel to the laminæ inside the crystal. From the measured inclination of the tilting stage, which should be the same as the angle which the light emerging from the crystal makes with the normal to the surface, the inclination i of the laminæ to the normal can be calculated. The relation between i and θ is obviously

$$\sin \theta = \mu \sin i,$$

where μ is the refractive index of the diamond (2·417), or the relative refractive index between the diamond and the surrounding medium (1·466), if the glass spheres with homogeneous immersion is used. The azimuth of the laminæ could also be measured by adjusting the tilting stage of the Federov rotation apparatus horizontal, and measuring the angle between the cross-wire and the reference line, *viz.*, one of the edges of the diamond.

The remarkable way in which the sharpening occurs can be seen from Figs. 2 (*a*) and (*b*) which represent the birefringence patterns of N.C. 124 when the diamond plate is normal to the axis of the microscope and is at the best position respectively. It will be seen that in the normal position there is practically no trace of the fine laminations, while on inclining the plate they come out prominently as fine sharp streaks. These photographs were obtained with the glass spheres, the tilting angle being 24°, which corresponds to an inclination of 16° 7′. It may be mentioned that X-ray measurements gave a value 16° for the inclination of the corresponding octahedral plane to the surface. (The surface was slightly inclined to an octahedral plane due to errors in polishing.)

The particular specimen of diamond referred to above was unique in that there was only one set of laminations shown in Fig. 2 (*b*). In general however, many diamonds exhibited laminæ parallel to 2 or 3 sets of octahedral planes and also sometimes to the dodecahedral planes. Details of these will be given in a later section on the results of the investigation.

Having thus determined the orientation of the laminations, the nature of the birefringence exhibited by them was next investigated. As already remarked, in the adjustments described above, the polariser and analyser were crossed, and they were rotated together until the required streaks in the

birefringence pattern were most clearly seen. It was found that the axes of the nicols made an angle of 45° to the direction of the laminations when this happened. If the nicols were now rotated together, a cycle of phenomena occurred, all the streaks vanishing when the axis of the polariser or analyser was parallel to them, and appearing in the intermediate positions. These observations clearly showed that the principal axes of birefringence in all the laminæ were parallel, and were respectively parallel and perpendicular to the intersection of the laminæ with the plane normal to the axes of the microscope. This phenomenon was found in all the cases of regular geometric birefringence. An illustration of the vanishing of the parallel streaks is provided by Figs. 3 (*a*) and (*b*). It will be seen that in both there is an irregular pattern which does not vanish at any setting of the nicols. But the regular parallel streaks vanish completely when the axis of the polariser or analyser is parallel to them.

To obtain more specific information regarding the nature of the birefringence in the laminæ, the following experiments were performed:

(i) Having verified that the axes of birefringence were parallel and perpendicular to the cross-wires in the sharpest position, the tilting stage was rotated so that the pattern was no longer sharp. Still the laminæ could be observed. Now also, on rotating the crossed nicols, extinction occurred four times in a revolution, respectively when the axes of the polariser and analyser were parallel to the cross-wire. This was found to be the case whatever be the angle through which the tilting stage was rotated.

(ii) The beam of light was also made to pass through the laminæ in different directions parallel to their plane, and the extinction directions were determined in each case. For this, the axis of the tilting stage was set perpendicular to the cross-wire, and by rotating the glass disc and inclining the tilting stage, the birefringence pattern was obtained as before in the sharpest position, but with the streaks running perpendicular to the cross-wire. The Federov stage was then rotated through an angle (say of about 20°) about the principal horizontal axis. The previous adjustments were repeated to obtain the streaks in the sharpest position and the effect of rotating the nicols was studied. It was found that now also the principal axes of birefringence were parallel and perpendicular to the lines in the birefringence pattern. The same was found to be the case for different settings of the crystal in which the light traversed it in various directions parallel to the laminæ.

From these experiments, one can conclude that *the laminæ behave like uniaxial crystals with the optic axis normal to them.*

4. Studies with the Babinet Compensator

The "order of birefringence" of the laminations, *viz.*, the difference in the refractive indices for vibrations along directions parallel and perpendicular to the optic axis, was determined by means of a Babinet compensator, which was relatively a simple matter since the direction of the optic axis was known from the previous studies. But the usual methods of determination with uniaxial crystals had to be modified to suit the purposes of the present investigation. This was so because one is interested here in the *variations* of the order of birefringence from place to place *over the area of the crystal plate*. The method employed could be described as follows. The crystal plate was first adjusted by means of the Federov stage so that the laminations were seen most clearly by the method of the previous section. The plane normal to the direction of propagation of the light within the crystal then contained the optic axis (which was perpendicular to the cross-wire, the laminations being parallel to it). The crossed polariser and analyser were rotated to extinguish the laminations, and were then set accurately at 45° from this position. By the transverse motion of the microscope stage the diamond plate was moved off the field of the microscope. The Babinet compensator was put in with its length parallel to the cross-wire, the analysing nicol was removed and the eye-end nicol put on the compensator and adjusted to $-45°$. The bands in the compensator should then be at right angles to the cross-wire. The diamond was then moved into the field, when *a focussed image of the diamond was thrown on the plane of the quartz wedge of the compensator*. Then it was found that the bands in the field of view of the compensator were not straight, but assumed a zig-zag shape. This occurs because the phase difference between the two polarised components varies from place to place, and the displacement of the Babinet fringes parallel to the cross-wire is a measure of this relative phase difference. Fig. 2 (*d*) is the photograph of what happens to the Babinet fringes with the diamond N.C. 124, the same specimen which was described in the last section in connection with the study of the laminations. This pattern might be called the "Babinet pattern" and gives a picture of the distribution of the magnitude of the birefringence over the area of the crystal plate. It may be mentioned that in this photograph, as well as in the photograph of the laminæ under crossed nicols [shown in Fig. 2 (*b*)], the microscope could not be focussed sharply over the whole field of view on account of the inclination of the crystal. Only a portion was accurately focussed.

If t is the thickness of the plate, i the inclination of the laminations to the normal to the surface, and if ϵ is the phase difference and μ_1 and μ_2 the principal refractive indices, then

$$\epsilon = 2\pi (\mu_1 - \mu_2)\, t/\lambda \cos i \text{ or } \Delta\mu = \mu_1 - \mu_2 = \epsilon\lambda \cos i/2\pi t.$$

$\Delta\mu$, the order of birefringence, is thus directly proportional to the phase difference and hence to the displacement of the Babinet fringes from their zero position.

It will be noticed that the fringes have two types of displacements—one varying slowly over the length and breadth of the crystal, and the other having a rapid fine variation. The former is irregular and on a large scale; it must be attributed to accidental strains, etc., which gives rise to the irregular birefringence. The latter is what we are interested in; in this diamond, it is characterised by the fact that the Babinet fringes alternately go one way and the other about the mean position. This means that $\Delta\mu$ in the laminæ is alternately positive and negative, that is to say, the alternate laminæ behave as positive and negative uniaxial crystals. Anticipating a little from a later section, it may be remarked that the obvious explanation of this is that the alternate layers are under tension and compression. The fine variations assume different shapes in other diamonds; these and their interpretation will be discussed in the next section.

The effect of tilting the diamond away from the sharp position is much more pronounced with the Babinet pattern than with the birefringence pattern. The fine variations all vanish and the appearance of the fringes with N.C. 124 kept normal to the light is as shown in Fig. 2 (*d*). The contrast between this and Fig. 2 (*c*) is striking. So also, the sharp peaks seen in Fig. 4 (*d*) vanish in Fig. 4 (*b*) when the diamond is made normal. This phenomenon explains why the birefringence pattern is so confused when viewed normally in many of the diamonds.

5. Description of the Results

As a result of the observations on a number of diamonds, it was found that they could be divided into a few typical classes, as far as their behaviour in the polarisation microscope was concerned. We shall briefly describe the properties of these in general, illustrating them by one or two examples.

(i) First, there is the variety of diamond completely transparent to the ultraviolet upto 2250 Å.U. The birefringence patterns of these diamonds, when viewed normally, invariably show a large restoration of light and often contain sets of streaks running in different directions. It is found that, in every case, laminations are present parallel to either octahedral or dodecahedral planes, or both, and that they can be brought out prominently by the technique described above. There may be only one set of laminations, as for example in N.C. 124 shown in Fig. 2. The appearance of this diamond

when viewed normally under the polarisation microscope is shown in Fig. 2 (*g*). It will be seen that, apart from the fact that all the broad bands run in the same direction, there is no suggestion of the fine laminæ brought out so strikingly in Fig. 2 (*h*) by appropriate methods of observation. Figs. 2 (*a*) and (*b*) are photographs of the same phenomenon under greater magnification using the glass spheres of the Federov stage. This was the only diamond in the collection of Sir C. V. Raman which exhibited laminations in one direction only. All the other diamonds of this type had laminæ running in different directions, *e.g.*, with N.C. 126 three such sets could clearly be seen. These are illustrated in Figs. 3 (*d*), (*e*), (*f*) when in their sharpest position, descriptions of which are given in the legends accompanying the photographs. To illustrate the accuracy with which the orientation could be fixed, the table below gives the readings obtained for three diamonds with the microscope, which could be compared with the values to be expected for octahedral and dodecahedral planes from X-ray measurements. The X-ray values for the azimuth are correct only to 5° while those for the inclination are correct to a degree.

TABLE I

	N. C. 124		N. C. 125				N. C. 126			
	a	*i*	*a*	*i*	*a*	*i*	*a*	*i*	*a*	*i*
Birefringence ..	61°	15° to 17°	53°	18° to 21°	23°	−5° to 5°	48°	18° to 20°	−11°	18° to 21°	−42°	−5° to 5°
X-ray ..	60°	16°	50°	19½°	20°	0°	50°	19½°	−10°	19½°	−40°	0°
Parallel to ..	(111)		(111)		(110)		(111)		(111)		(110)	

In every one of the cases, the axes of birefringence were parallel and perpendicular to the laminations. The disappearance of the laminæ when the axis of the polariser or the analyser is made parallel to them is illustrated by Figs. 3 (*a*) and (*b*). It will be noticed that in Fig. 3 (*b*), which was photographed with the polariser parallel to the laminæ, the bright streaks in Fig. 3 (*a*) have completely vanished.

With all the diamonds, the Babinet pattern has the zig-zag shape described in the previous section. It is most pronounced in N.C. 124 which has only one set of laminæ.

(ii) The birefringence patterns of some ultra-violet opaque diamonds consist of a dark field crossed by a small number of bright streaks. An examination of such diamonds with the Federov stage showed that the streaks invariably had their origin in thin laminæ running parallel to octahedral planes. They sharpen up remarkably when tilted so that the light

passes parallel to them, as may be seen for example from Figs. 4 (*a*) and (*c*), which are the photographs of the appearance of one set of laminæ in N.C. 94 when viewed through the polarising microscope normally and in the sharpest position respectively. The axes of birefringence in laminæ of this type were also found to be parallel and perpendicular to the laminations. The Babinet patterns are very interesting. It is found that, corresponding to every one of the laminations, the dark fringe of the Babinet compensator has a sharp hump on one side or the other. Two such humps towards the right hand side may be seen in Fig. 4 (*d*) corresponding to the two bright streaks in Fig. 4 (*c*) with diamond N.C. 94. There are six such sets of laminæ running along the sides of a hexagon in N.C. 94, and with every one of them the hump was towards the right. However, with the lamina found in N.C. 99, illustrated in Fig. 4 (*e*), the hump was to the left. It is not uncommon to find some laminations producing humps on one side and some on the other in the same diamond. For example, in B 1 two laminæ quite close by produce displacements of the Babinet fringe on opposite sides. The photograph of the laminæ in the sharpest position is shown in Fig. 4 (*g*) and their Babinet pattern is reproduced below them in Fig. 4 (*h*).

The humps in the Babinet pattern disappeared when the diamond was tilted away from the correct orientation, as for example in Fig. 4 (*b*). In general, it was found that the displacement of the Babinet fringe was greater with a thinner lamina than with a thicker one. It may also be remarked that the broad lamina in N.C. 99 is ultra-violet transparent. Rendall (1944) has obtained a streak of transparency in this position in the ultra-violet transparency pattern. Presumably, the streaks in the other diamonds are also transparent, but being very thin and lying obliquely to the surface of the diamond, it is difficult to verify whether they are transparent or not. By using a technique similar to that employed in the present investigation, *viz.*, by holding the diamond at the appropriate angle to the beam of ultra-violet light, it may be possible to detect the transparency of these laminations.

(iii) In a large number of ultra-violet opaque diamonds, a restoration of light sometimes accompanied by one or more series of bands was found when viewed normally under crossed nicols. These diamonds were generally yellow luminescent, the bands of yellow luminescence running parallel to those in birefringence (Rendall, 1946). These plates, when viewed at the proper angle with the Federov stage, exhibited a series of laminations running in one or more directions, generally parallel to the octahedral planes. The axes of birefringence were parallel and perpendicular to the laminæ. The Babinet pattern had in general a number of humps,

some going one way and some the other way, the displacement, however, being smaller than with those classed under (i). These diamonds could be considered as being very similar to those in (ii), but in which a large number of laminæ occur.

(iv) There were a few diamonds of the ultra-violet opaque class, which exhibited only pure blue luminescence and which produced very little restoration of light under crossed nicols. These failed to show any laminations under the experimental conditions adopted by the author.

It may not be out of place here to give some idea of the thickness of the laminæ as also of the order of birefringence produced by them. Both were variable, and it is only possible to give the order of magnitude of the quantities. The laminæ had thicknesses varying from about $10\,\mu$ to $100\,\mu$ or a little more, being similar both in the ultra-violet transparent as well as the ultra-violet opaque diamonds. By using a standard quartz plate, it was found that a shift of the Babinet fringes to the right meant that the refractive index for vibrations parallel to the laminæ, μ_h, was less than that perpendicular to it (μ_v), and *vice versa* for a displacement to the left. Thus, if the laminæ behaves like a positive uniaxial crystal *i.e.*, $\Delta\mu = \mu_v - \mu_h$ is positive, then the shift will be to the right and *vice versa*. As already remarked, the displacement was either to the right or to the left in diamonds of the types (ii) and (iii), the magnitude varying from 0·5 mm. to about 2·5 mm. Allowing for the thickness of the diamond and the inclination of the light to the surface, these correspond to orders of birefringence of 0·00006 to 0·00031. With ultra-violet transparent diamonds, in which the Babinet fringe alternately goes one way and the other, the maximum relative displacement is about 5 mm., nearly double that found in the opaque diamonds. All these measurements are only rough and are intended only to give an idea of the orders of magnitude of the quantities concerned.

6. Discussion and Interpretation of the Results

As already remarked, many diamonds exhibit an irregular birefringence pattern produced as a result of flaws and accidental strains in the crystal, which gives rise to a coarse and irregular displacement in the Babinet pattern. We shall leave this aside and consider only the fine laminations which may be observed by the techniques described above.

The important points to be considered in this connection are that (*a*) the laminæ behave as uniaxial crystals with the optic axis along their normal and (*b*) as is seen from the behaviour of the Babinet fringes they may behave either as a positive or a negative uniaxial crystal. In ultra-violet opaque

diamonds, the laminæ usually occur interspersed in the bulk of the crystal, these producing either a positive or a negative hump in the Babinet pattern. On the other hand, ultra-violet transparent diamonds possess a laminated structure throughout their volume, the alternate laminæ being positive and negative. The obvious explanation for such a behaviour of the laminæ is that the birefringence is a photo-elastic effect produced as a result of stresses acting on them. If the photo-elastic constant were known it would be possible to calculate the magnitude of the stresses. Even in the absence of such information, it is possible to have an idea of the nature of the stresses. Assuming that the photo-elastic constant concerned is positive, it would mean that the positive laminæ are under compression and that the negative laminæ are under tension along a direction normal to them. In any case, *it is clear that the laminæ that occur in the ultra-violet opaque diamonds are of two classes*, viz., *those that are under compression and those that are under tension*. Similarly, the laminæ in the ultra-violet transparent diamonds are alternately under compression and tension.

As was mentioned in the last section, there is strong reason to suppose that the laminations found in the ultra-violet opaque diamonds are transparent. Since the intrusion of this variety sets up stresses which may be either tensile or compressive, it is reasonable to suppose that there are really two variants of the transparent type, which are both in some way (probably in their lattice spacing) different from the opaque type and also from one another. This would immediately explain why the laminæ in the ultra-violet transparent diamonds are alternately under compression and tension —the alternate laminæ are composed of the two different variants of this type.

All these deductions are beautifully in accord with the theory put forward by Sir C. V. Raman (1944) regarding the structure of diamond. According to this theory, diamond can have four possible structures, two of which, TdI and TdII, possess tetrahedral symmetry, while the other two, OhI and OhII, possess octahedral symmetry. The former two are physically identical, but differ only in orientation. They are infra-red active and are also opaque to the ultra-violet below 3000 Å.U. The latter two are, however, transparent to the ultra-violet upto 2250 Å.U. They are both geometrically and physically different from each other, as well as from the tetrahedral varieties. The differences, however, are so small that it is possible for the different structures to co-exist side by side in the same specimen of diamond.

If one studies these structures carefully (see for example Fig. 1 on p. 191 in the paper by Raman quoted above), it will be seen that the tetrahedral

structures are intermediate between the two octahedral structures. Thus, designating the two interpenetrating lattices of carbon atoms in the diamond structure by A and B, then starting from OhI, if one reverses the direction of the axes of all the atoms in the B lattice, one gets TdI (or reversing the axes of all the atoms in the A lattice, one would get TdII). After this, if the axes of the atoms in the A lattice are reversed (or of those in the B lattice in the latter case), one now obtains the OhII structure. Hence, it is reasonable to suppose that the two Td structures have properties intermediate between those of OhI and OhII.

For example, the lattice spacing of the tetrahedral varieties would be less than that of one of the octahedral structures (say OhI) and greater than that of the other (OhII). This is exactly what is required to explain the phenomena observed with the laminations. Thus, if a lamina occurring in the midst of tetrahedral ultra-violet opaque diamond consists of the OhI variety only, then its lateral dimensions would be larger than the surrounding, there being thus stresses along the two boundaries tending to decrease the area of the lamina. These stresses would be present along all directions in the plane of the lamina and are equivalent to a tensile stress normal to it. On the other hand, if the lamina consists of the OhII variety, then the stresses acting on it would be equivalent to a compressive stress normal to it. Thus, one of them would behave as a negative uniaxial crystal and the other as a positive one respectively, exactly as is found to be the case.

In the ultra-violet transparent diamonds, however, the OhI and OhII structures alternate in the laminations giving rise to compressive and tensile stresses in alternate laminations, as is in fact found. It also follows from the above argument that the difference in the birefringence and hence the relative shift of the Babinet fringes for an octahedral lamina in a tetrahedral diamond should be about half that between the two alternate laminæ in an octahedral diamond. That this is roughly the case is shown by the measurements reported in a previous section.

The small magnitude of the birefringence, *viz.*, less than 1 in 10,000, shows that the differences in the properties of the four diamond structures should be very small. This fits in with the results deduced by the author (1946) regarding such differences from X-ray and other data. Thus it is in concordance with the fact that the infra-red absorption coefficient of the tetrahedral diamonds is very small compared with other infra-red active crystals (Ramanathan, 1946). So also, these ultra-violet opaque diamonds have a relatively small absorption coefficient upto 2250 Å.U., the transmission extending upto this wavelength with thin plates. The results of the present

investigation thus lend great support to Raman's theory. In particular they show very clearly that there are two variants of octahedral diamond, a result which is a direct outcome of the theory.

7. Laminations in Luminescence

Raman (1944 *b*) has pointed out that bands of yellow luminescence often appear sharp and clearly defined when viewed at certain angles and diffuse at others. This must be due to the fact that the luminescence is located in laminæ having a definite orientation. An attempt was made to see whether the technique of using the Federov stage can be used to bring out the laminæ in luminescence. The difficulty was that the diamond had to be sufficiently luminescent to be seen under the microscope. However, the phenomenon sought for was found. Figs. 5 (*a*) and (*b*) represent respectively the luminescence of diamond N.C. 154 when seen normally and in oblique position at which the bands are sharpest. Owing to the depth of focussing being small, only a few sharp bands are seen in Fig. 5 (*b*). The laminæ were verified to be parallel to a set of octahedral planes.

In conclusion, I wish to thank Sir C. V. Raman for the encouraging interest that he took in the investigation.

Summary

The birefringence patterns of many plates of diamond show sets of bright parallel streaks which have been attributed to the existence of definitely orientated laminations inside the crystal which are under strain. These laminæ are most clearly seen when the light beam is made to pass parallel to them inside the crystal, which has been achieved in the present investigation by the use of a Federov stage and a polarising microscope. By properly inclining the plate of diamond placed on the Federov stage, it is found possible to observe the laminary structure even in diamonds which do not exhibit any streaks when viewed normally. From measurements made with the Federov stage and with X-rays, the orientation of the laminæ was fixed. The laminæ are in general parallel to octahedral or dodecahedral planes. The same specimen of diamond may possess laminations in more than one direction, each of which appears prominently when viewed properly. Quantitative studies of the birefringence of the laminæ have also been made with a Babinet compensator. The studies show that the laminæ behave either as a positive or a negative uniaxial crystal, with the optic axis normal to them. They usually have a thickness between 10μ and 100μ and the order of birefringence varies from $0{\cdot}00006$ to $0{\cdot}0003$. In ultra-violet opaque diamonds, octahedral laminæ of the transparent diamond are found, which

have either positive or negative birefringence, laminæ of both types being sometimes present in the same specimen. On the other hand, the ultra-violet transparent diamonds are completely laminated, the alternate laminæ being positive and negative. These observations support the ideas of Raman that there are two varieties of the ultra-violet transparent diamond which are different from each other and from the opaque type. Also, it is seen that one of them has a larger and the other a smaller lattice spacing than the opaque diamond. Laminæ having a definite orientation have also been found to be exhibited in luminescence.

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Description of the Plates

Fig. 2. (*a*) Birefringence pattern of N.C. 124 when viewed normally, taken with the glass hemispheres of the Federov stage × 28.

(*b*) Ditto when viewed at the proper inclination × 28. Note that the laminæ which come out so prominently in this are practically unobservable in (*a*).

(*c*) Babinet pattern corresponding to (*a*) × 20.

(*d*) Ditto corresponding to (*b*) × 20.

(*e*) Babinet pattern of same diamond at smaller magnification, covering practically the whole of the diamond, at normal incidence, taken without the glass spheres ×10.

(*f*) Same as (*e*) at the sharpest position × 10.

(*g*) Birefringence pattern of N.C. 124 showing the whole diamond at normal incidence × 5.

(*h*) Ditto at the proper inclination × 5.

Fig. 3. (*a*) Birefringence pattern of one of the laminations in N.C. 125 at the sharp position with the axes of polariser and analyser at 45° to the laminæ × 10.

(*b*) Ditto with the axis of the polariser parallel to the laminæ × 10. Note that the fine streaks have disappeared.

(*c*) Babinet pattern corresponding to (*a*) × 25.

(*d*) Photograph of a set of dodecahedral laminæ (the thin horizontal streaks) in N.C. 126 × 7·5.

(*e*) Photograph of a set of octahedral laminæ × 7·5. These are the same as the coarse vertical bands seen in (*d*), but in the sharp position.

(*f*) Photograph of a third set of laminæ parallel to the octahedral planes in this diamond × 7·5.

FIG. 4. (*a*) Birefringence pattern of a portion of N.C. 94 viewed normally × 10.

(*b*) Babinet pattern of the same × 10.

(*c*) Birefringence pattern at the proper inclination of the region shown in (*a*) × 10. Note the sharpness of the laminæ.

(*d*) Babinet pattern of (*c*) × 10. Note the humps in the fringes going to the right.

(*e*) A broad lamina in N.C. 99 at the sharp position × 10.

(*f*) Babinet pattern of (*e*) × 10. The hump here goes to the left.

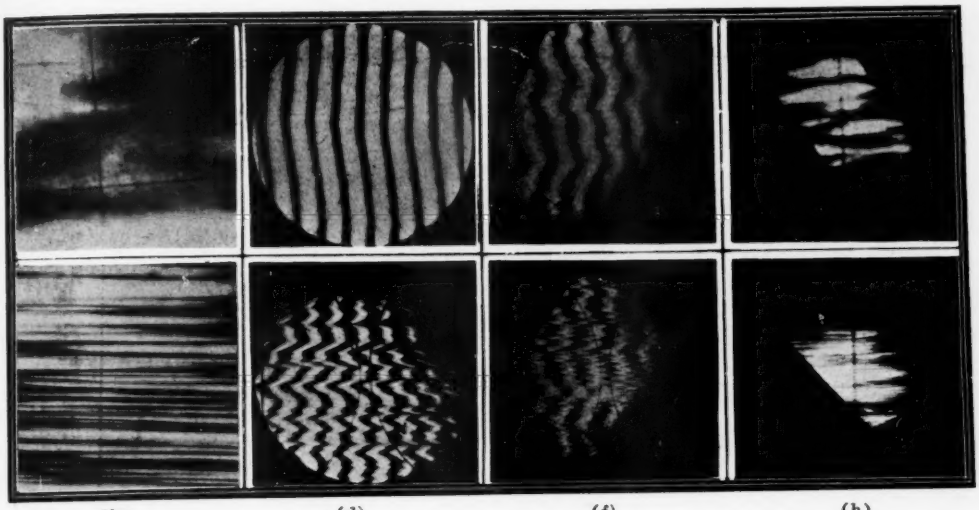
(*g*) Two laminæ in diamond B.1 at the sharp position × 28.

(*h*) Their Babinet pattern. One hump goes to the right and the other to the left × 20.

FIG. 5. (*a*) Luminescence pattern of N.C. 154 when viewed normally × 10.

(*b*) Ditto at the correct inclination for a set of octahedral planes × 10. A few laminæ are seen sharply.

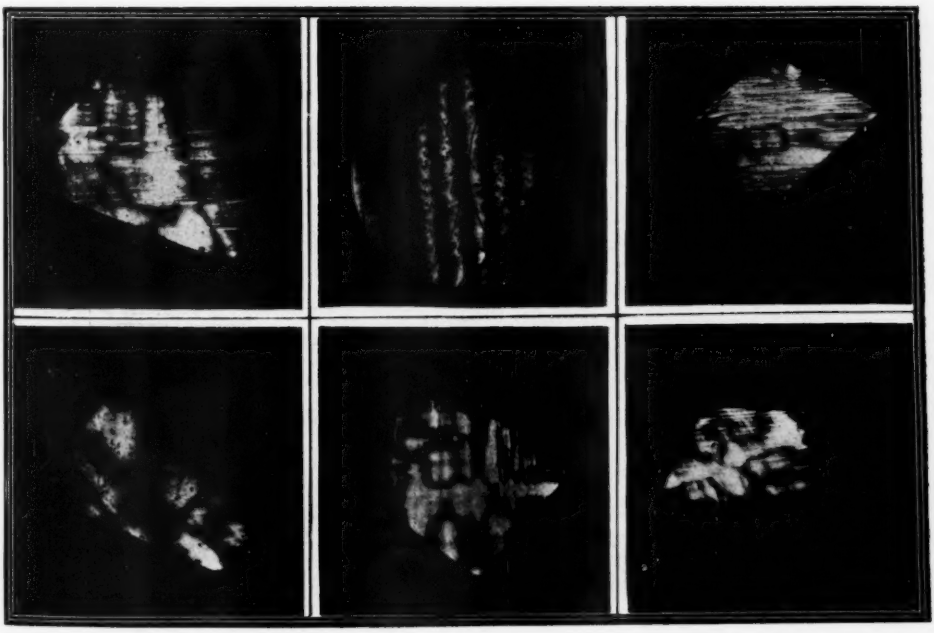
(a) (c) (e) (g)



(b) (d) (f) (h)

FIG. 2

(a) (c) (e)



(b) (d) (f)

FIG. 3

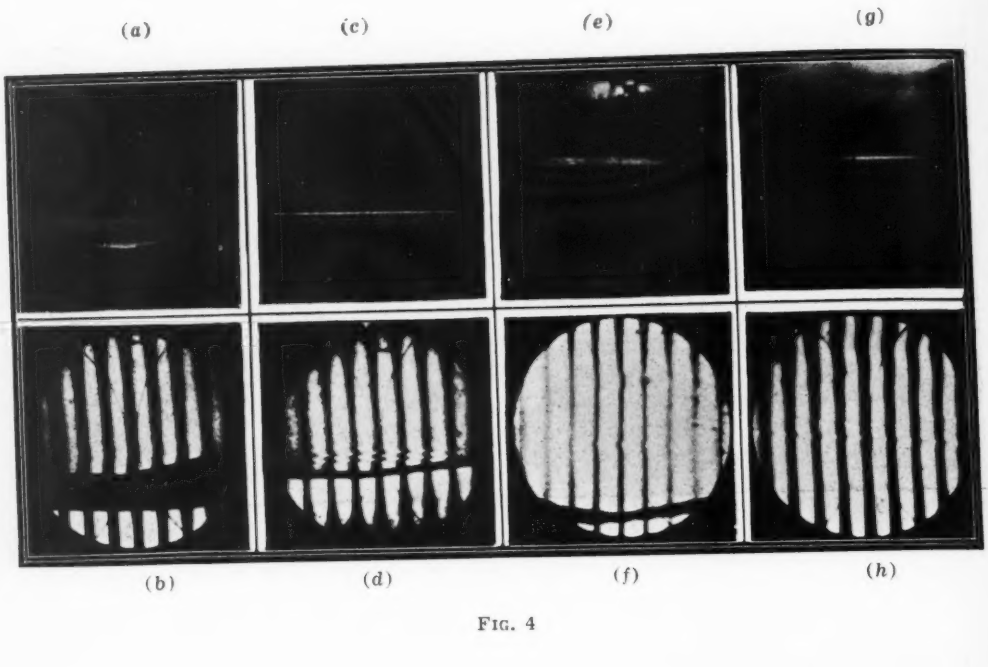


FIG. 4

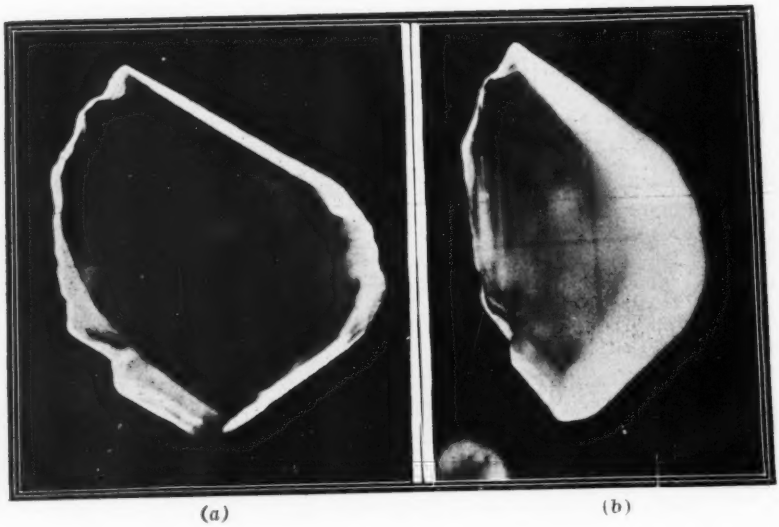


FIG. 5

THE LUMINESCENCE OF DIAMOND EXCITED BY X-RADIATION

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1. Introduction

Diamond can be made to luminesce in a variety of ways, *e.g.*, by irradiating with ultra-violet rays, cathode rays or X-rays or by the action of heat or friction. The fluorescence spectra and various other properties associated with fluorescence, such as the local variations of colour and intensity, have been studied by a number of workers in this laboratory using ultra-violet excitation (Nayar, 1941; Mani, 1944, 1945; Sunanda Bai, 1944; Rendall, 1946). John (1930) has reported a study of the fluorescent spectrum when exposed to cathode rays. The present paper describes the investigations made by the author on the fluorescence of diamond when irradiated with X-rays. Among the various phenomena that were studied may be mentioned the fluorescence spectra, the fluorescence patterns, the correspondence or otherwise of these with those produced by ultra-violet excitation and the influence of the hardness and intensity of X-rays on the intensity of luminescence. A discussion is also included on the probable mechanism by which the luminescence is produced by the impact of X-rays.

2. Colour and Intensity of Luminescence

The luminescence of diamond under X-ray irradiation is much weaker than that under ultra-violet irradiation. The X-ray tube was generally run at 10 to 15 milliamperes with a peak voltage of 35 K.V. Preliminary observations showed that increasing the voltage applied to the X-ray tube remarkably brightened up the luminescence. Consequently, voltages up to 50 K.V. were used for feebly luminescent diamonds. A tungsten target was used in the X-ray tube to have a high efficiency of production of X-rays.

Visual observation with a large number of diamonds showed that the colour of luminescence in X-rays generally followed the colour as seen in the ultra-violet. The diamonds which fluoresced blue in ultra-violet rays were also blue in X-rays, but the colour in X-rays had less of violet in it. The colour was blue to blue-green. Similarly, diamonds fluorescing green in ultra-violet also showed a green colour in X-rays. The so-called non-

luminescent diamonds which emitted practically no light in ultra-violet rays were definitely luminescent in X-rays, although the luminescence was very feeble. The colour could not be fixed definitely on account of the extreme feebleness, but appeared to be blue to blue-green.

A striking fact that was obvious even on visual observation was that the range over which the intensity of luminescence varied from specimen to specimen with X-ray irradiation was much smaller than with ultra-violet irradiation. This phenomenon was demonstrated in a qualitative manner by a series of photographs taken by the author and published in a paper by Sir C. V. Raman on the " Nature and Origin of Luminescence in Diamond " (Raman, 1944). The photographs were taken with a jewel containing a large number of diamonds which were known to fluoresce in ultra-violet rays with intensities varying in the ratio of about 1 : 1000. (Photographs illustrating this fact were also reproduced in Sir C. V. Raman's paper quoted above). With X-rays, the maximum range was certainly not more than 1 : 50. This phenomenon was quantitatively studied in a particular case of a purely blue-fluorescent diamond (N.C. 100) which showed patches of luminescence, which were sensibly uniform in intensity, but whose intensities were different. Since the diamond was of uniform thickness, complications due to differences in thickness did not arise. The diamond had at least three distinct areas whose intensities of luminescence were different (see Fig. 6), which may be designated by A, the central bright patch, B, a small extension of this triangular patch to the right and C, the feebly luminescent surrounding area. The relative intensities of luminescence of these three areas were determined by photographic photometry. An absorption cell of a solution of sodium nitrite in water was always kept in front of the camera to absorb the ultra-violet rays scattered by the diamond. This cell was also kept when photographing the luminescence excited by X-rays, so that the comparison of intensities was restricted to the spectral region of luminescence in the visible. The results of photographic photometry gave intensity ratios of 12 : 5·0 : 1 with ultra-violet excitation, while with X-rays it was only 2·5 : 1·6 : 1. The interpretation and explanation of this fact will be taken up in a later section.

3. Luminescence Patterns of X-ray Luminescence*

All diamonds which exhibited patterns of luminescence when excited by ultra-violet rays were found to exhibit patterns under X-ray excitation

* Hereafter, by the term 'X-ray luminescence' will be meant the luminescence under X-ray excitation, and similarly 'ultra-violet luminescence' will mean the visible luminescence excited by ultra-violet rays.

also. The patterns were photographed with some diamonds. The technique was very simple. The diamond was kept in a light-tight box, one side of which was closed by black paper, through which X-rays were incident. The diamond was kept at an angle of about 30° to the X-ray beam and the pattern was photographed with a camera whose axis was kept normal to the diamond plate. An examination of the appearance of the patterns in the focal plane of the camera confirmed the fact that the colour of the luminescence with X-rays is very much the same as with ultra-violet rays. The luminescence patterns observed were also found to be remarkably similar to those in ultra-violet luminescence. Hence, only a small number of photographs were taken to illustrate the patterns. These are reproduced in Figs. 5 and 6 in Plate VIII. No attempts were made to separately photograph the blue and yellow luminescence patterns by the use of filters, as even the total luminescence took many hours to photograph and since the resemblance of these to the corresponding patterns in ultra-violet luminescence was so striking. However, it was found that the X-ray luminescence patterns were less contrasty than the ultra-violet luminescence patterns of the same diamond. This will be evident on comparing the X-ray luminescence pattern of N.C. 100 (Fig. 6) with the corresponding ultra-violet luminescence pattern reproduced in a paper by Rendall (1946) in this symposium. The origin of the difference must be found in the result described in the preceding section, namely that the ratio of intensities of luminescence had a much smaller range when X-rays are used than when ultra-violet rays are used. The same phenomenon was also observed with other diamonds.

It was observed that if the diamond plate was kept very nearly parallel to the X-ray beam so that the X-rays entered it at grazing incidence, then the details in the luminescence pattern became very much clearer and sharper than otherwise. This will be evident from Fig. 5 which is the luminescence pattern of N.C. 118 using X-rays falling at an angle of 5° on the diamond. If one compares it with the corresponding pattern in ultra-violet light (reproduced as Fig. 10, D. 198 in Sir C. V. Raman's paper quoted earlier), it will be seen that the X-ray luminescence pattern is by far the clearer and the sharper of the two. The origin of this sharpening must be traced to two causes. Firstly, the bands of bright luminescence in diamond are generally found to be located in fairly narrow laminæ parallel to the octahedral planes (Ramachandran, 1946). In diamonds of octahedral cleavage, these laminæ do not run normal to the surface of the diamond, so that if the whole thickness of the diamond is luminescent, the luminescence pattern becomes somewhat confused when viewed normally. The second fact to be considered is that the luminescence with X-rays is largely caused by

the soft components which are absorbed in a relatively small distance from the surface. The proof of this fact will be given in the next section. Therefore, when the diamond is kept obliquely to the X-ray beam, the intense part of the luminescence is confined to a thin layer near the front surface, and the confusion arising in the pattern due to overlapping is avoided. The pattern thus comes out sharp and clear.

As already remarked, diamonds which do not luminescence in ultraviolet light are definitely luminescent in X-rays. The intensity is very small, about one-twentieth of the weakest blue-luminescent diamond, but it can be seen clearly. In Fig. 6 the X-ray luminescence pattern of such a diamond (N.C. 60) is reproduced. It will be seen that there is little variation in intensity. The bright lines near the corners are due to bevelled edges, and the series of rings near the centre are interference fringes produced at the contact between the diamond and the plate on which it was kept.

4. Effect of the Quality and Intensity of X-Rays on the Intensity of Luminescence

The influence of the applied voltage and the current through the X-ray tube on the intensity of fluorescence was investigated by photographic photometry. All the photographs were taken with the same exposure time, and no assumptions were made as to the approximate validity of the reciprocity relation. The time of development and other factors were carefully controlled. The diamond employed for the investigation was N.C. 73, which exhibited uniform blue luminescence. The density of the photographs was measured by a Moll microphotometer and the standards were obtained by varying the aperture of the camera. The results of the studies are given in Tables I to III below, which give respectively the effect of current and voltage applied to the X-ray tube and the effect of interposing aluminium filters of known thickness.

Table I

Effect of current through the X-Ray tube on the fluorescence intensity. Applied peak voltage 45 K. V.

Current m. amp.	Intensity of fluorescence in arbitrary units
1·0	1·0
2·5	2·4
5·0	5·1
8·0	7·9
10·0	10·0

TABLE II

Effect of the voltage applied to the X-Ray tube on the fluorescence intensity. Current 5 m.amp.

Peak voltage in K. V.	Fluorescence intensity I in arbitrary units	Log I
52·5	16·6	1·22
45·0	7·4	0·87
37·5	5·5	0·74
30·0	3·2	0·50
22·5	1·6	0·21
15·0	0·27	T·44

TABLE III

Effect of interposing aluminium foils in the X-Ray beam on the total intensity of fluorescence I of the diamond. Applied peak voltage 35 K. V.

Thickness *t*	I	Log I
mm.		
0·0	5·0	0·70
0·2	2·2	0·34
0·4	1·35	0·13
0·55	1·0	0·00

It will be seen that the intensity of fluorescence varies linearly with current over the range of intensities studied. It may be remarked that the absolute intensity was very much smaller than that excited by ultra-violet light, so that such an accurate linearity is to be expected. The photometry confirms the visual observation that an increase in the applied voltage has an appreciable enhancing influence on the fluorescence intensity. It will be seen that, in the range 25 to 50 K.V., an increase in peak voltage of 7·5 K.V. nearly doubles the intensity of fluorescence. If log I were plotted against the logarithm of the voltage, it will be found that the resulting curve is nearly a straight line with a slope of about 3, so that the fluorescence intensity varies roughly as the cube of the voltage. This will be considered in greater detail in a later section. The results in Table III are very interesting since they throw much light on the relative capacities of X-rays of different wavelength to excite fluorescence in diamond. The fact that the intensity is reduced to less than half by the interposition of only 0·2 mm. of aluminium, which transmits more than 60% of all wave-engths below 0·9 Å.U., shows that components softer than this play a

predominant part in exciting the fluorescence. This point is considered in greater detail in a later section where quantitative formulæ for the intensity of luminescence are developed.

In order to confirm this fact, namely that most of the fluorescence is excited by soft X-rays, the following experiment was conducted. A diamond (N.C. 71) which had a long straight edge was kept with this edge facing the X-ray tube and in such a way that the X-rays passed exactly parallel to the broad sides. In this way, the X-rays which excited the fluorescence entered through the edge over an area defined by the length and thickness of the crystal and proceeded inwards along its breadth. If the diamond were viewed in a direction at right angles to the X-rays, a shading away of the luminescence from the front edge inwards was observed, as was expected. The softer components of the X-rays were completely absorbed within the first millimetre or so, and the luminescence was very bright near the front edge. As the X-rays progressed inwards they became harder and harder so that the intensity of luminescence steadily decreased. The phenomenon was photographed and the photograph is reproduced in Fig. 7 (*a*), Plate IX. To further confirm the idea, aluminium foils of different thickness were introduced between the diamond and the X-ray tube. It was then observed that the intensity of luminescence fell down progressively, as was to be expected from the results described in the previous para. But what was more interesting was the fact that the fading away of the luminescence from the front surface inwards was also less and less prominent. These are illustrated by Figs. 7 (*a*) to (*d*), which were taken with aluminium foils of thicknesses 0·0, 0·1, 0·2 and 0·55 mm. interposed. The exposure times were 1 hr., 2 hrs., 4 hrs. and 8hrs. in order to obtain approximately the same initial intensity at the front edge. It will be seen that the fall of the luminescence intensity is less and less prominent as one passes from Fig. 7 (*a*) to (*d*). The corresponding microphotometric traces are also reproduced in Fig. 1 which show very clearly that the rate of falling away of the intensity of fluorescence is smaller when the incident X-rays are made harder. Also, a study of the slope of the microphotometric traces at different distances from the front edge shows that this also becomes smaller and smaller as one goes away from this edge. The reason for this becomes clear if one notes that the softer X-rays are also absorbed by the diamond, so that the X-ray beam becomes harder as it progresses into the crystal, and is consequently absorbed less. The quantitative calculations are reserved to a later section.

The falling away of the intensity of luminescence as the X-rays penetrate the crystal was visually observed also with N.C. 60, a diamond of the ultra-violet transparent variety.

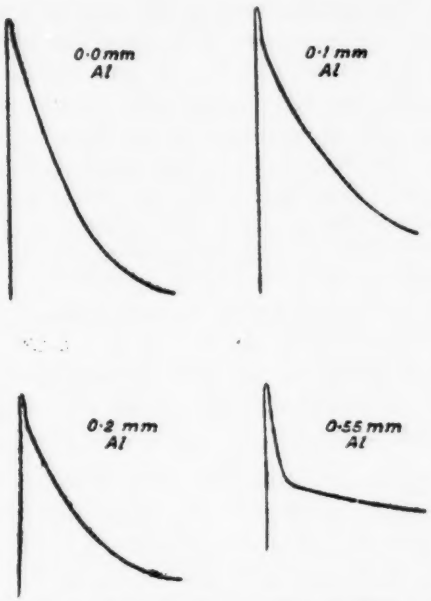

FIG. 1. Microphotometric traces of the fall of fluorescence intensity. These were copied from the original traces to facilitate reproduction as line blocks

5. X-RAY LUMINESCENCE SPECTRUM OF DIAMOND

Since the luminescence of diamond under X-ray irradiation is extremely weak, a study of the spectrum was made with a fast spectrograph of small dispersion. A somewhat detailed study has been made only with one diamond, N.C. 68, which is intensely blue-luminescent when excited by ultraviolet rays. In X-rays, it was weakly luminescent, so that long exposures had to be given to obtain the spectrum. An idea of the relative intensities in the two cases may be obtained from the fact that while 5 minutes sufficed to give a strong spectrum in the former case, an exposure of 20 hours was necessary to get a moderately strong spectrum with X-rays. The two spectra have been taken side by side with a Hartmann diaphragm and are reproduced in Fig. 8. These were taken at room temperature. A comparison of the two spectra shows that, on the longer wave-length side of the principal electronic line at 4156 Å.U., the spectrum is essentially the same in both the cases, namely consisting of four emission bands with maxima at 4278, 4387, 4514 and 4643 Å.U. The intensity of the bands are, however, different in the two cases. The spectrum of the X-ray luminescence in this region

appears as though the emission bands are superposed on a continuous spectrum. The most interesting fact that comes out of the comparison of the two spectra is that, while the 4156 line itself comes out as an *emission* line in ultra-violet fluorescence, it occurs as an *absorption* line in X-ray fluorescence. Also, there is an extension of the spectrum to the shorter wavelength side of 4156 Å.U. in X-ray fluorescence, which is absent with ultra-violet excitation. This extension occurs as a continuous spectrum, in which the absorption bands occur with maxima of absorption at 4041, 3950 and 3850 Å.U. The continuous spectrum extends upto about 3600 Å.U. These details can be seen in Fig. 8, Plate IX. The spectrum of X-ray luminescence can thus be described as a combination of the absorption and the ultra-violet luminescence spectra. It is a continuous spectrum, on which the absorption of diamond acts for wavelengths smaller than and including 4156 Å.U. and on which is superposed the ultra-violet fluorescence bands for longer wavelengths.

That this description is essentially correct is shown by a study of the two spectra given by a weakly blue-fluorescent diamond, N.C. 73. The ultra-violet fluorescence spectrum of this diamond is exactly similar to that of N.C. 68, except for the fact that the whole spectrum is fainter. The X-ray luminescence spectrum, on the other hand, is strikingly different. It consists of a continuous spectrum running from about 3600 to 5000 Å.U. with just a hint of an absorption line at 4156 Å.U. The continuous spectrum was recorded with nearly the same exposure as was required for N.C. 68 (*viz.*, 20 hours), but no quantitative estimate was possible since the two diamonds had very different sizes and shapes. Since this diamond (N.C. 73) was feebly absorbing in the near ultra-violet, the absorption bands did not occur in the spectrum. It thus appears as though X-rays give rise to a continuous spectrum in all diamonds of the blue-fluorescent class, and in addition give rise to the characteristic fluorescent bands with an intensity proportional to the intensity of ultra-violet fluorescence. This idea fits in qualitatively with the results obtained for the two diamonds described above. For instance, it explains why the bands in the X-ray fluorescence spectrum are less clear than in the ultra-violet fluorescence spectrum with N.C. 68 and why they are absent in that of N.C. 73.

A more quantitative verification of this idea is obtained in an entirely different manner, namely from the results described in section 2, in particular the values for the relative intensities of luminescence of different regions of N.C. 100 under X-ray and ultra-violet excitation. Let i_0 be the intensity of the continuous spectrum given by X-rays and let i be the intensity of the

fluorescent spectrum given by ultra-violet light. Then the intensity of fluorescence under X-rays is

$$I = i_0 + ki \tag{1}$$

according to the above ideas. If we denote by subscripts 1, 2, 3 the three areas of the diamond showing different intensities of luminescence, then

$$\frac{I_3}{I_1} = \frac{i_0 + ki_3}{i_0 + ki_1} = \frac{K + i_3}{K + i_1}, \text{ putting } \frac{i_0}{k} = K \tag{2}$$

In arbitrary units, we have $I_3/I_1 = 2{\cdot}5$ and $i_3 = 5{\cdot}0$, $i_1 = 1{\cdot}0$, so that K comes out to be $6{\cdot}33$. Substituting the values for i_1 and i_2 and K in

$$\frac{I_2}{I_1} = \frac{K + i_2}{K + i_1}, \qquad \frac{I_2}{I_1} = 1{\cdot}78 \tag{3}$$

which is in fairly good agreement with the experimentally determined value of $1{\cdot}6$ given in section 2. So also, this idea makes it intelligible why the maximum range of luminescence intensities is only 1 : 50 with X-rays while it is as large as 1 : 1000 with ultra-violet.

6. Mechanism of the Production of Luminescence by X-rays

In section 4, the results of experiments were described, which show how the intensity of luminescence varies with the intensity and hardness of the X-rays, the voltage applied to the X-ray tube and so on. A quantitative explanation of these results must be sought for in a theory of the mechanism of the production of the luminescence. It is obvious that the luminescence cannot be the direct outcome of the absorption of X-rays, for this results only in the ejection of photoelectrons which are of very high energy (of the order of tens of kilovolts) compared with energies of the order of a few volts associated with the luminescence. These photoelectrons are, however, rapidly absorbed in the medium as a result of the ionisation they produce. It is these low energy ions that are responsible for the production of luminescence.

Using these ideas, it is possible to deduce an expression for the intensity of luminescence. Let $u_\lambda\, d\lambda$ be the intensity of X-rays at the point concerned in the spectral region λ to $\lambda + d\lambda$ and let a_λ be the fraction of this absorbed per unit length in the medium. a_λ is obviously equal to $\rho\mu_\lambda$, where ρ is the density and μ_λ the mass absorption coefficient. Then the amount of X-rays absorbed per unit area in a thickness dt of the medium is clearly $a_\lambda i_\lambda d\lambda dt$, which is obviously proportional to the number of photoelectrons produced. This is not exactly true, since part of the X-rays absorbed is due to scattering and to the Compton effect. The assumption is, however, approximately true, particularly for the longer wavelengths. Now, the photoelectrons

produced by the X-rays are absorbed within such a short distance (of the order of 0·01 mm.) that it is reasonable to assume that they are absorbed as soon as they are produced* with the formation of low-energy ions. However, the number of ions so produced should depend on the energy of the photoelectron. Since the production of each ion requires, on the average, a certain energy, we may suppose that the total number of ions produced is proportional to the energy of the photoelectron, *i.e.*, is inversely proportional to the wavelength of the X-ray, since the difference in energy between the X-ray and the photoelectron is only a few electron volts (the K absorption limit for carbon corresponds to an energy of 284eV), which is small ($< 2\%$) compared with energies of the order of thousands of electron volts for the X-ray. Consequently, if one takes the intensity of fluorescence I at any point to be proportional to the number of ions per unit volume generated at that point, then

$$I = K \int_{\lambda_m}^{\infty} \frac{a_\lambda u_\lambda}{\lambda} d\lambda, \text{ where K is some constant} \qquad (4)$$

We shall now apply this general formula to calculate the variation of the intensity of fluorescence with various factors and compare it with the experimental results described above. The integral in (4) was evaluated by numerical integration, by dividing the range of wavelengths into a large number of sections and substituting the values of a_λ, u_λ and λ for each. The spectral variation in the intensity of white X-rays given out by a tungsten target has been studied by a number of investigators, but the only set of results covering a wide range of voltages which was found useful for the calculations were those given by Ulrey (1918). Although these have not been corrected for the variations in the structure factor of the crystal, etc., they form a fair basis for the calculations, which are themselves expected to be not very accurate. Besides, no data as to the intensity of the characteristic radiation under the same conditions are available and so no account was taken of the characteristic radiation. The data for white radiation were corrected for absorption in the window of the X-ray tube, which set the upper limit for λ at 3 Å.U. The values of the absorption coefficients were taken from standard tables (*e.g.*, Compton and Allison, 1935) and were obtained by interpolation.

* This is easily proved. If the X-rays are absorbed with an absorption coefficient a and the photoelectrons with a coefficient b with the formation of a tertiary product (ions), then the concentration of this tertiary product at a distance x from the boundary of the medium can be shown to be practically proportional to the intensity of the primary X-rays for values of $x > (\log b/a) / (b - a)$. Actually, for diamond this comes out to be 0·01 to 0·02 mm. for the X-rays used in these studies.

(*a*) *Variation in the intensity of fluorescence with the distance from the front edge when the diamond is kept with its edge towards the X-ray tube.* It is easily seen that the intensity at a distance x cms. from the edge is

$$I_x \propto \int \frac{i_\lambda \, a_\lambda}{\lambda} \, exp\,(-a_\lambda \, x)\, d\lambda \qquad (5)$$

where $i_\lambda d\lambda$ is the intensity of white X-rays emerging from the X-ray tube in the range λ to $\lambda + d\lambda$. The theoretically calculated values are represented as the continuous curve in Fig. 2, while the circles are the experimetnal values obtained from the first microphotometric trace in Fig. 1. The agreement is seen to be remarkably good, except for the first point, which is much above the theoretical curve. This is obviously due to the presence of the characteristic L-radiation of tungsten in the region 1·0 to 1·5 Å, of which no account is taken in the theory. These are absorbed to a very large extent in the first 0·1 cm. and practically completely in 0·2 cm.

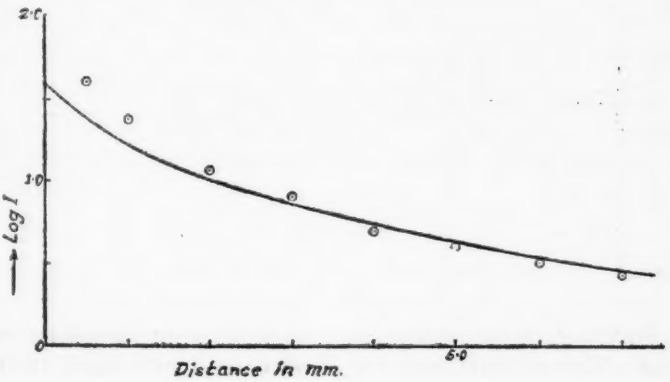

FIG. 2

(*b*) *Variation of the intensity with voltage.*—Under the experimental conditions, it is the total luminescence produced in the full thickness of the diamond that matters. Consequently, one must consider the total amount of X-rays of each wavelength that is absorbed in the diamond while calculating the luminescence intensity. Obviously this is proportional to $i_\lambda \{1 - exp\,(-a_\lambda l)\}$, where l is the length of the path traversed by the X-rays in the medium. If the diamond is kept at an angle θ to the X-ray beam, $l = t$ cosec θ where t is the thickness of the crystal plate. Hence,

$$I_V \propto \int_{\lambda_m}^{\infty} \frac{i_\lambda}{\lambda} \{1 - exp\,(-a_\lambda \, l)\}\, d\lambda \qquad (6)$$

Both the lower limit of integration and i_λ vary with the voltage. The results of the calculations for a number of voltages are represented as a continuous curve in Fig. 3, in which log I_V is plotted against log V. The experimental data are shown by crosses against the corresponding values of the R.M.S. voltage. The agreement with theory is satisfactory. For the lowest voltage, however, the experimental point is appreciably above the extrapolated theoretical curve. This can be explained to be due to the presence of characteristic radiation, the relative proportion of which is larger for smaller voltages, as in the present case.

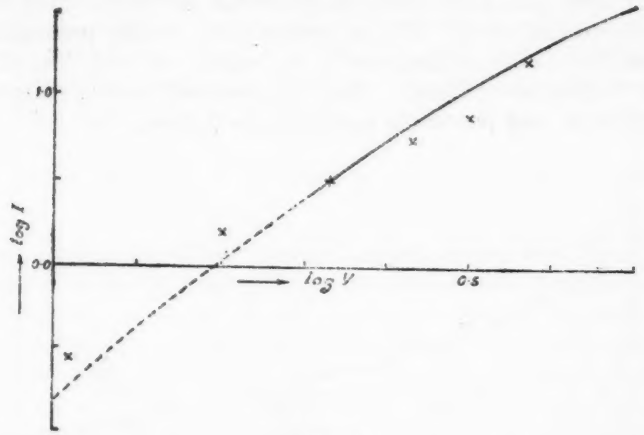

FIG. 3

(c) *Reduction in the luminescence intensity when aluminium foils are introduced.*—With an aluminium foil of thickness T introduced, the formula for the intensity is

$$I_T \propto \int_{\lambda_m}^{\infty} \frac{i_\lambda}{\lambda} \{1 - exp(-a_\lambda\, l)\}\, exp(-b_\lambda\, T)\, d\lambda \qquad (7)$$

where b_λ is the linear absorption coefficient for aluminium. The results of calculations made with formula (7) are shown in Fig. 4. The agreement with experiment is reasonably good in this case also.

These calculations thus support the idea that the production of luminescence by X-rays should be considered to be a tertiary phenomenon, namely, originating as a result of the ionisation produced by the photoelectrons ejected by the primary X-rays. Of course, the recoil electrons produced by the Compton scattering should also produce luminescence;

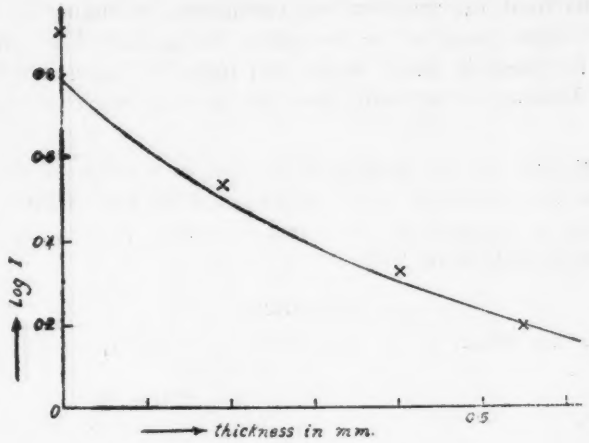

FIG. 4

but the contribution due to these is comparatively small for X-rays which are not very hard, as were used in these experiments.

My sincere thanks are due to Prof. Sir C. V. Raman for the suggestion of the problem and for the discussions I had with him during the course of the investigation.

SUMMARY

The paper deals with the investigations carried out by the author on various phenomena connected with the luminescence of diamond excited by X-rays. The fluorescence generated by X-rays was found to be much weaker and also to vary over a smaller range of intensities than that excited by ultra-violet light. The colour as well as the patterns of luminescence were the same as those excited by ultra-violet light, except that the patterns had less of contrast. By photographic photometry, the fluorescence intensity was found to be directly proportional to the current through the X-ray tube and to vary roughly as the cube of the voltage. Experiments are described which show that soft X-rays are more effective in producing luminescence than hard X-rays.

The luminescence spectrum of a brightly blue luminescent diamond excited by X-rays consisted of bands on the longer wavelength side of 4156 Å.U., these coinciding with those in the spectra excited by ultra-violet light, but there was a continuous spectrum on the shorter wavelength side, which was crossed by the absorption bands of diamond. The principal electronic line at 4156 Å.U. occurred as an absorption line. With a weakly blue-

fluorescent diamond, the spectrum was continuous, extending on either side of 4156 Å.U. with a trace of an absorption line at 4156 Å.U. A probable explanation for these is given, which also makes it intelligible why, with X-rays, the fluorescence intensity does not vary as much as with ultra-violet rays.

It is suggested that the luminescence arises as a result of the ions produced by the photoelectrons which are ejected by the X-rays. On this basis, quantitative formulæ are developed to explain the experimental data, and are found to hold fairly well.

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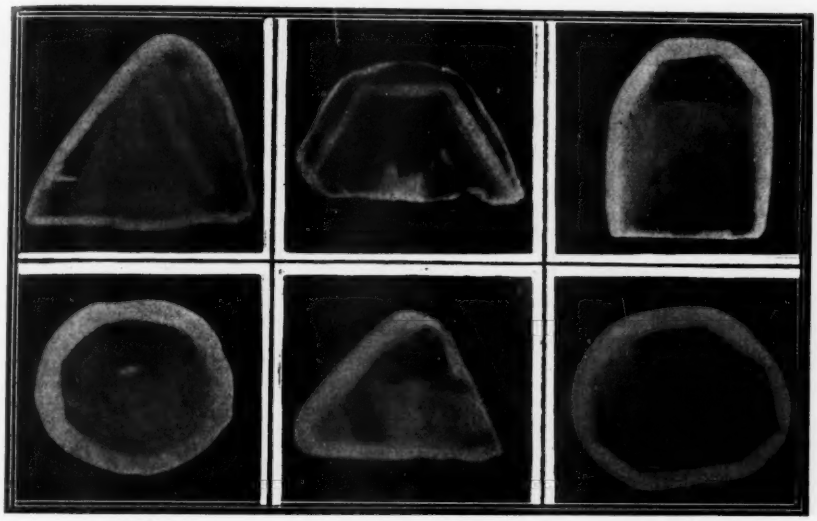
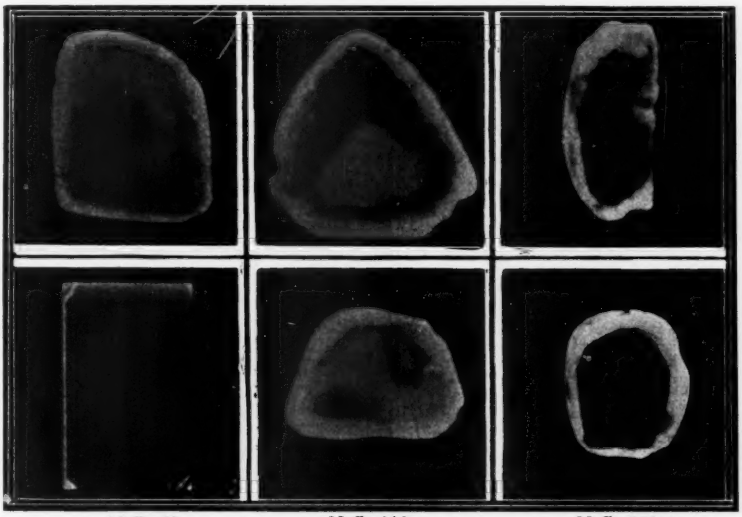
N.C. 115 N.C. 118 N.C. 82



N.C. 80 N.C. 88 N.C. 99

FIG. 5. X-Ray Luminescence Patterns

N.C. 127 N.C. 100 N.C. 122



N.C. 60 N.C. 111 N.C. 120

FIG. 6. X-Ray Luminescence Patterns

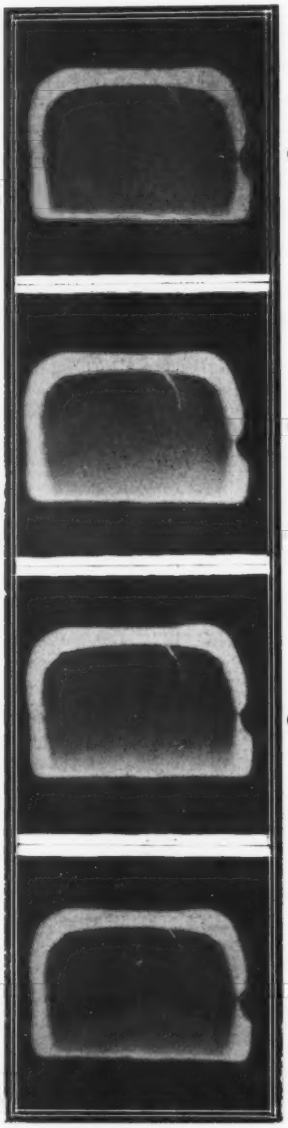


FIG. 7. For explanation see text

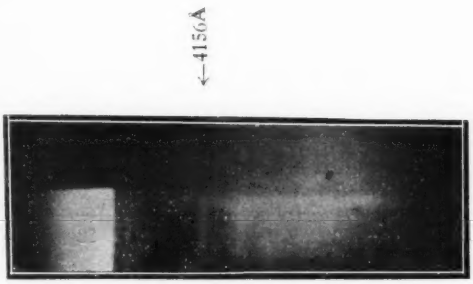


FIG. 8

Luminescence Spectrum of N.C. 73 with

(*a*) X-Ray excitation and

(*b*) Ultra-Violet excitation

X-RAY TOPOGRAPHS OF DIAMOND—PART II

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

In an earlier paper by the author (1944 *a*) bearing the same title, a method was described by which it is possible to obtain a photographic reproduction (X-ray topograph) of the variations in the X-ray reflecting power over the area of a cleavage plate of any crystal. The method consists in using white X-rays diverging from a pinhole and obtaining Laue reflections from the full area of the cleavage plate. The reflections may be obtained either from the internal or surface crystallographic planes. In the former case, the crystal and the photographic plate have to be kept inclined at definite angles to the X-ray beam to obtain a non-distorted picture of the crystal, the values of which for any experimental arrangement could be obtained from formulæ given in the earlier paper. When X-ray reflections are obtained from the surface cleavage plane, it is only necessary to keep the photographic plate parallel to the crystal to obtain a perfect reproduction. A number of X-ray topographs obtained by the former method were reproduced in the paper quoted above and were discussed. These topographs were, however, defective for two reasons. Firstly, since duplitized X-ray films were used, two images were produced which were not in register on account of the oblique incidence of the X-ray beam on the film. This seriously affected the clarity of the topographs. It was found that the use of photographic plates eliminated this defect, although this necessitated the giving of fairly long exposures. Using this technique, some of the cleavage plates of diamond studied earlier have been reinvestigated and new specimens have also been studied. The other defect in the earlier photographs arose out of the use of fairly thick specimens. Since internal reflections were invariably involved, the reflections given by different layers of the diamond parallel to the surface were superimposed, thus obliterating many of the fine details (*e.g.*, lines and streaks) lying parallel to the plane of incidence and emphasizing those lying perpendicular to it. This defect was appreciably reduced by the use of thin plates. Five such thin specimens, N.C. 151, N.C. 155, N.C. 156, N.C. 160 and N.C. 162 have been studied. The clarity of the photographs obtained

with the new technique makes more precise observations possible. The present paper embodies the results of such further studies made on the X-ray topographs of diamond. In particular, the crystallographic orientation of the various bands and streaks found in the X-ray topograph is discussed and the significance of the topographs in relation to the various other patterns exhibited by diamond is brought out.

Since the publication of the previous paper by the author on the subject, a note has appeared in *Nature* by N. and W. A. Wooster (1945) describing their experiments for obtaining topographs using the principle of Bragg reflection from the surface. The author wishes to point out that the possibility of obtaining topographs using the surface reflection from a stationary crystal was envisaged in the earlier paper (1944 a) where it was stated that, in this case, "the condition for no distortion is extremely simple, namely that the film must be parallel to the crystal." The surface reflection method was not used by the author since the reflected X-rays were even more obliquely incident on the film than in the other method and would completely mask all details if duplitized films were used. The method has later been tried with photographic plates, and the surface topographs thus obtained were essentially the same as those produced by internal reflection. An advantage of the ingenious modification of the method by N. and W.A. Wooster, in which the crystal and film are simultaneously oscillated and the characteristic X-radiation is employed, is that the exposure times are reduced very much.

2. Crystallographic Orientation of the Plates Studied

Most of the specimens studied were of octahedral cleavage. However, it is interesting to note that a few diamonds were found in the collection of Sir C. V. Raman which were cleavage plates with their faces parallel to the (211) plane. N.C. 82, for instance, whose topograph is reproduced in this paper, is one such diamond. It is a fairly large plate (8 mm. × 10 mm.) having a thickness of about 2 mm. N.C. 60 is a rectangular block 10 mm. × 6 mm. × 1·5 mm. whose broad faces are parallel to the (211) plane, while the two edges are respectively parallel to (111) and $(01\bar{1})$ planes. N.C. 178 is another specimen whose broad faces are parallel to the (211) plane. The large size of these diamonds and the fact that the orientations of the surfaces were found to differ by less than 1° from those of the crystallographic planes suggest that these plates should have been obtained by cleavage. The slight deviations are to be explained as due to errors in polishing. These facts suggest that *diamond has a cleavage parallel to the* {211} *planes*, although this is not as often observed as the octahedral cleavage.

3. Interpretation of the Topographs

In the previous paper by the author (1944 *a*), it was mentioned that any increased reflection that is observed must be attributed to mosaic structure, arising from the angular deviation of fine crystallites in a sub-microscopic scale from their mean orientation. It is a point of interest to find out whether this is really the case, or whether there is a misorientation of fairly large layers or blocks in the crystals. In another investigation, the author (1944 *b*) has studied the angular divergence of the X-ray reflections given by blue-luminescent diamonds and has found that the reflection from the (111) planes had an angular half-width of nearly 60 seconds in an intensely luminescent diamond while it was only 3″ with a feebly luminescent diamond. The measurements were made on the Bragg reflections obtained from the surface of a stationary crystal using X-rays diverging from a very fine slit. The line obtained on the photographic plate was very regular and of uniform width, showing that the mosaic structure is on a very fine scale. When the same technique was tried with a non-luminescent diamond of the ultra-violet transparent variety, it was found that the line was very much distorted. The width of the reflected X-ray beam was of the order of a few minutes of arc, and the distribution of intensity over the width was highly irregular, the $K\alpha_1$ and $K\alpha_2$ lines being not at all resolved. These phenomena suggest that, in this variety of diamonds, misorientations on a fairly large scale also occur.

The question can also be settled in another way, namely by taking distortionless topographs at different distances from the crystal. This is best accomplished by obtaining topographs using surface reflections and keeping the photographic plate parallel to the surface of the crystal, when one obtains a slightly enlarged non-distorted image. In practice, this was done by having a long arm capable of rotating about the axis of the crystal, and setting this at double the angle of reflection to the direct beam of X-rays. The film-holder was kept at the requisite angle to the arm and by moving it towards or away from the crystal along it, topographs at various distances were obtained. It may be remarked that errors in the angular setting of the arm and the film holder would produce the same amount of distortion in all the pictures, so that the comparison can be done exactly. If the relative distances of the various streaks remain the same in all the topographs, then there is no gross misorientation, while the measurement of differences in these relative distances, if any, would give the angular tilting.

Actually, no such tilting could be found in the ultraviolet opaque diamonds showing blue luminescence, while a small angular tilting of a few minutes of arc was found in some ultraviolet transparent diamonds. This

probably explains why the latter class of diamonds give very much more intense X-ray reflections and why, in some cases, the Laue spots are drawn out into curious shapes. The topographs reproduced do not give a true representation of the relative intensities of reflection given by different diamonds, for the exposure times were adjusted so as to get approximately the same density in all the cases. An idea of the enormously greater intensity of reflection given by the ultraviolet transparent diamond may be obtained from the fact that N.C. 125 in Fig. 1, which belongs to this class, required only an exposure of 15 minutes, while the topograph of N.C. 100 in the same figure, which is a diamond opaque to the ultraviolet, required as much as 10 hours' exposure.

4. Discussion of the Topographs

For the purpose of this discussion, we shall consider not only the topographs reproduced in this paper, but also those reproduced in the earlier paper by the author (1944 *a*). Where reference is made to a diamond studied earlier, the new catalogue (N.C.) numbers are also given. For a proper appreciation of the discussion below, it will be useful to compare the topographs with the luminescence, ultraviolet transparency and birefringence patterns of the same diamond reproduced in a paper by Rendall (1946) appearing in this symposium.

It is convenient to divide the diamonds that were studied into three classes:

(*a*) those exhibiting pure blue luminescence,

(*b*) those that are non-luminescent

and (*c*) those exhibiting both blue and yellow luminescence.

(*a*) As was remarked in the earlier paper, the topographs of purely blue-luminescent diamonds, which are opaque to the ultraviolet below 3000 Å.U. did not exhibit any streaks but only areas of varying intensity, these corresponding closely with those occurring in luminescence. N.C. 100 whose topograph is shown in Fig. 1, Plate X, is a good example. The central bright portion here corresponds exactly with the bright region in the luminescence pattern. The central bright area has, in addition, a weaker extension to the left in the luminescence pattern, which is also correspondingly reproduced in the X-ray topograph. In the case of other diamonds of this class like D 36 (N.C. 71), D 45 (N.C. 72) and D 221 (N.C. 73) studied earlier, both the luminescence pattern and the X-ray topograph are uniform. There is thus no doubt that, in diamonds of the blue-luminescent class, the X-ray reflecting power increases with increasing intensity of luminescence.

(*b*) In contrast to the above class of blue-luminescent diamonds, there is a class which transmits down to 2250 Å.U., and which does not exhibit any luminescence, examples of which are N.C. 124, N.C. 125 and N.C. 126. A characteristic feature of the X-ray topographs of these diamonds is the existence of sets of parallel streaks.

As has been shown by the author in another paper (Ramachandran, 1946) appearing in this symposium, diamonds of this class possess a laminated structure, the laminations being generally parallel to octahedral planes and less often to dodecahedral planes. It is of interest to know if the streaks found in the X-ray topographs also represent these laminæ. A study of the directions of the streaks showed that they were invariably parallel to the intersection of either an octahedral or a dodecahedral plane with the surface. However, if the laminæ observed optically are very fine and closely spaced, then the corresponding streaks are not found in the X-ray topograph. This is the case, for example, with N.C. 124 (D 207), which reveals fine laminæ under the polarising microscope. These lines, however, are absent in the topograph. The reason why this happens is that the reflection takes place not only from the surface of the crystal plate but also from the interior. Consequently, the streaks get superposed on one another and they disappear, if they are very fine. For the same reason, details consisting of lines running perpendicular to the plane of reflection are lost, while those parallel to it come out clearly. This is why only one set of streaks running at about 30° to the horizontal is found in the topograph of N.C. 125 in Fig. 1. These correspond to dodecahedral laminations seen under crossed nicols. Optically, octahedral laminations running perpendicular to these have been observed; but they are not found in the topograph since they are at right angles to the plane of reflection. With N.C. 126 (D 209), only a coarse pattern is observed in the topograph, presumably due to misorientations. The laminations are very fine and are not found in the topograph.

(*c*) The most interesting class of diamonds, in so far as the relationship between X-ray topographs and other patterns is concerned, is that which exhibits both blue and yellow luminescence. A number of such diamonds have been studied in detail and most of the topographs reproduced in this paper belong to this class. These diamonds can again be subdivided into two varieties, *viz.*, (i) those in which the blue and yellow luminescence patterns are identical and (ii) those in which they are different. To the former class belong N.C. 113 shown in Fig. 1, N.C. 156 and N.C. 160 in Fig. 2 and N.C. 80 (D 38 of author's earlier paper). In all cases, it is found that the topograph and the birefringence pattern follow the luminescence pattern, parallel bands occurring in the topograph in the same places as in

luminescence. In N.C. 113, there are also large variations in ultraviolet transparency, the two margins being more transparent than the rest of the diamond. These correspond with the bright bands seen in the topograph in the same regions.

The latter class is even more interesting, typical examples of which are N.C. 115, N.C. 82, N.C. 108 and all the diamonds in Fig. 2 except N.C. 156 and N.C. 160. As a result of a comparison of these topographs with the other patterns of the same diamonds, the following general results may be stated:

(1) The bands of yellow luminescence have their counterpart in the topograph.

(2) Also, these bands correspond to the lines found in the birefringence pattern, the similarity between the topograph and the birefringence pattern being generally very striking.

(3) Variations in blue luminescence are not generally reproduced in the topographs.

(4) Although the blue luminescence pattern shows a great similarity to the ultraviolet transparency pattern, bright areas in the one corresponding to dark areas in the other, no particular similarity is observed between the topograph and the transparency pattern.

These may be illustrated with special reference to the diamonds whose topographs are reproduced in Figs. 1 and 2. The blue luminescence pattern of N.C. 115 consists of a central triangular bright patch with dark areas surrounding it near the margins. The ultraviolet transparency pattern has an inverse relation to this, as described above. The X-ray topograph does not show these differences, but the three bands found in the yellow luminescence pattern are beautifully recorded in it. There is also some similarity to the birefringence pattern.

N.C. 82 exhibits exactly similar features, the blue luminescence and transparency patterns corresponding inversely, while the yellow luminescence pattern is different, namely consisting of bands running diagonally. The latter are found both in the X-ray topograph and the birefringence pattern.

The blue luminescence pattern of N.C. 155 is practically uniform, while parallel bands are seen in both the yellow luminescence and birefringence patterns. These correspond exactly with the fine bands found in the X-ray topograph. (It may be noted that the diamond is inverted in the topograph with respect to the other patterns, right side here corresponding to left in the others and *vice versa*.)

N.C. 151 is another typical case in which the blue and yellow patterns are quite different. The birefringence pattern consists of bands running parallel to the yellow luminescence pattern and the topograph also shows these same bands. As will be seen from the topograph, there is some sort of discontinuity in the middle of the diamond. This could be seen visually in the birefringence pattern also when the nicols are oriented properly.

The patterns of N.C. 108 are rather confused, but still a general similarity is observable between the various patterns.

5. Interpretation of the Results

A theoretical background on the basis of which one may attempt to interpret the above results is furnished by Sir C. V. Raman's theory (1944) of the ultimate structure of diamond. According to Sir C. V. Raman, diamond can have four different structures. Two of these, called TdI and TdII, have tetrahedral symmetry, and by virtue of the selection rules exhibit an absorption for infra-red radiation in the region of 8μ. They are physically identical with each other, differing only in their geometrical orientation. The other two structures, OhI and OhII, possess octahedral symmetry and are consequently transparent to the infra-red. They are however, distinct from each other and also from the tetrahedral varieties. The various structures may exist side by side in the same specimen of diamond and it is the differences in the nature and the extent of interpenetration of the various structures that produces the amazing variations in the properties of diamond.

The blue luminescent diamonds on account of their infra-red absorption, should consist solely of the TdI and TdII varieties. According to Raman's theory, blue luminescence arises from the intermixture of these two varieties, the intensity being determined by the extent of their interpenetration. Although the two structures are physically identical, nevertheless there would be discontinuities at the places where they join with each other, so that a sort of mosaic structure should result, the magnitude of the mosaicity being larger, the more intimately the two structures are mixed. These considerations give a satisfactory explanation of the direct correlation observed between the intensity of X-ray reflection and that of blue luminescence.

The non-luminescent diamonds are transparent both to the ultra-violet below 3000 Å.U. and to the infra-red in the region of 8μ. These should therefore consist only of the OhI and OhII varieties. The two structures are physically different and consequently one would expect the diamond to be subject to severe strains. In fact, in another paper appearing in this symposium, the author (1946) has shown that the lattice spacings of the two

structures are different, that the diamond consists of laminæ alternately made of OhI and OhII structures and that these laminæ are alternately under compression and tension. It is therefore not at all surprising that these diamonds possess a large mosaic structure and that they often show gross misorientations.

The other type of intermixture that is possible is that between a Td and an Oh structure. Raman supposes that, in this case, yellow luminescence results. This is supported by the author's observations on the laminations in such diamonds. If, in the midst of a blue-luminescent diamond, a yellow streak is observed, then it is found that birefringence is produced at this region and that the diamond composing the thin lamina has either a larger or a smaller spacing than the bulk of the specimen. (For further details, see the paper by the author quoted above.) Thus, at places where a band of yellow luminescence is observed, there should be a comparatively large mosaic structure, since the structure there has a spacing different from the rest of the crystal, in contrast with the areas of blue luminescence where the two intermingling structures are of identical lattice spacing. This explains why yellow bands are invariably represented in the topograph as bright streaks while variations in blue luminescence are not represented.

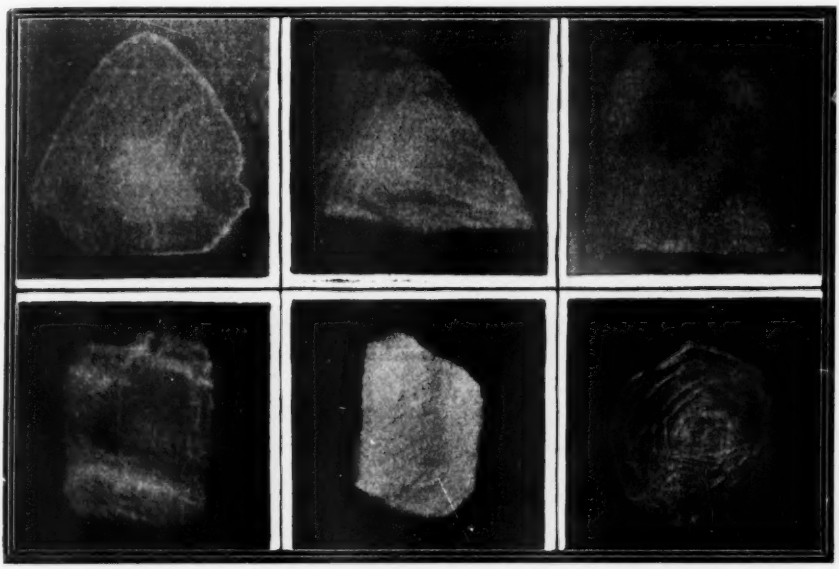
The facts described in the previous section thus find a reasonable explanation on the basis of Raman's theory.

I wish to express my indebtedness to Sir C. V. Raman for the constant encouragement that he gave me during the course of this investigation.

Summary

X-ray topographs (*viz.*, photographic representations of the variations in the X-ray reflecting power over the area of a crystal plate) of a number of diamonds have been obtained and studied. Comparing these with the other patterns of the same diamonds, the following results emerge: (1) In purely blue-luminescent diamonds, there is a direct correlation between the intensity of luminescence and the X-ray reflecting power. (2) Topographs of non-luminescent diamonds show parallel bands, which often correspond with the bands in the birefringence patterns. They also suggest that gross misorientations of fairly large crystalline blocks sometimes occur in these diamonds. (3) In diamonds showing both blue and yellow luminescence patterns, the topograph exhibits a correspondence only to the yellow luminescence pattern if the two are different, and to both if they are similar. An explanation of these results is given on the basis of Raman's theory of the structure of diamonds.

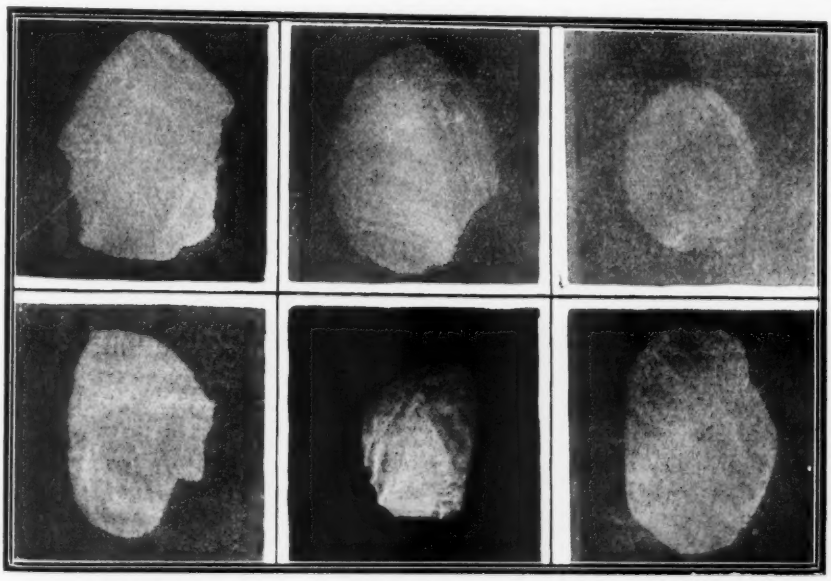
N.C. 100 N.C. 115 N.C. 82



N.C. 125 N.C. 113 N.C. 108

FIG. 1. X-Ray Topographs of Diamond

N.C. 155 N.C. 156 N.C. 162



N.C. 114 N.C. 160 N.C. 151

FIG. 2. X-Ray Topographs of Diamond

A study of the orientation of a number of cleavage plates made in connection with this investigation showed that although most of them were of octahedral cleavage, at least 3 of the diamonds had their *large* faces parallel to the (211) plane, showing that diamond has also a direction of easy cleavage parallel to the {211} planes.

Note added on 17*th June* 1946.—Since the above was written, it has been discovered by Ramaseshan (1946) that diamond possesses many other cleavages besides the new one (211) reported in section 2 of this paper. Consequently, a systematic study of the orientation of a number of diamonds in the collection of Sir C. V. Raman was undertaken to see if any of the cleavage plates belonged to any of these new classes. Out of a total of 48 diamonds studied, it was found that 42 were of octahedral cleavage. Of the remaining, 3 diamonds (N.C. 60, 82 and 178) had their surfaces parallel to a {211} plane, N.C. 88 was parallel to a {322}, N.C. 123 to a {320} and N.C. 174 to a {431} plane. The orientation of the last one was not very definite, since it was less than 5° away from a {331} or a {321} plane. The fact that such large cleavage plates having a surface area of 20 sq. mm. and above could be obtained parallel to these planes is very striking. It shows that the cleavages are fairly well-defined, and thus supports the findings of Ramaseshan.

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THE FARADAY EFFECT IN DIAMOND

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1. Introduction

Since diamond is optically isotropic and has a large dispersive power, it may be expected to show an easily observable Faraday effect. A search of the literature however reveals only a single observation on the Faraday effect of diamond recorded by H. Becquerel (1877) in the following words, "In a remarkable crystal (octahedral) belonging to M. Fizeau, we obtained a feeble rotation of near about 27 minutes in yellow light." The thickness of the specimen was 2·875 mm. and the effective field was 7330 gauss. The Verdet's constant for diamond calculated from these data comes out as 0·0128 minutes per centimeter per gauss. This is actually less than that constant for common crown glass and, as we shall see in the course of the paper, it is only one-half of the correct value. The lack of any further observations with diamond in the century which has elapsed since Faraday's original discovery is evidently due to the difficulty of obtaining suitable specimens for study. As is wellknown, diamond commonly exhibits birefringence in greater or less measure, and the restoration of light due to this effect when the crystal is observed between crossed nicols completely overpowers the feeble restoration due to the action of the magnetic field. That Becquerel could at least observe the Faraday effect shows that the particular specimen was better than most samples. The low value obtained by him may be ascribed to the difficulty of measuring the Faraday effect in the presence of residual birefringence. Indeed, the Faraday rotation in isotropic bodies is known to be markedly diminished in the presence of birefringence induced by strain (Schutz, *Magneto Optik*, 1936).

However, contrary to the belief that has been frequently expressed in recent literature, birefringence is *not* always to be observed in diamond. The observations of Raman and Rendall (1944) on this point indicate that it is present only when there is an admixture of physically different allotropic modifications of diamond and is absent when there is no such admixture. In Sir C. V. Raman's collection of crystals and of cleavage plates, there are several specimens of diamond of which the birefringence is negligibly small.

Amongst these, the cleavage plates N.C. 157, N.C. 177 and N.C. 73 having approximately parallel faces were found on examination to be suitable for Faraday effect studies. The thickness of these plates were however rather small (0·58, 0·85 and 0·68 mm. respectively). Observations were also possible with a large diamond crystal in its natural form, N.C. 4, which gave an easily observable Faraday rotation on account of its considerable thickness (4·8 mm.). Owing, however, to the curvature of the faces of this crystal and the consequent deviation of the rays in passing through it, the magnitude of the Verdet's constant deduced from it is not as trustworthy as that deduced from the observations on the other three plates in spite of their comparatively smaller thickness.

Darwin and Watson (1927) have shown that the Faraday effect in most transparent bodies is accurately expressed by the modified Becquerel formula

$$V = \gamma \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}$$

where V is the Verdet's constant (rotation per cm. per gauss), e and m are the electronic charge and mass respectively, c is the velocity of light, λ the wavelength of the light used and n the refractive index of the substance. γ is a multiplying constant which may be called the *magneto-optic anamoly*. (γ is usually expressed as a percentage). As has been shown by Darwin and Watson, γ remains constant over the whole of the visible and near ultra-violet spectrum, provided the part of the dispersion associated with the infra-red absorption is eliminated from the dispersive power appearing in the formula. The value of γ for the great majority of carbon compounds lies between 40% and 60%. Accordingly in the present investigation, the Faraday rotation has been determined for different regions in the visible spectrum to determine the magneto-optic anamoly of diamond and to ascertain whether or not it is independent of the wavelength of the light employed.

2. The Experimental Procedure

The magnetic field.—A large electromagnet of the Rutherford type capable of giving fields upto 23,000 gauss was used for these investigations. Each of the two pole pieces supplied by the manufacturers had a longitudinal hole about 2 cms. in diameter. When the pole pieces are brought quite close, the large size of the holes would result in the field between them being low and also sensibly non-uniform. To eliminate this difficulty, specially designed soft iron plugs were introduced which reduced the diameter of the holes to 0·6 cm. The pole pieces after this modification, had a flat area of about 2 sq. cms. They were kept at a distance of 0·95 cm. apart. A

measurement of the field with a small search coil and fluxmeter over various regions in the space between the pole pieces showed that the variations in the field along the lines of force were not greater than 2 to 3 %. The magnitude of the field with 6 amps. current through the exciting coils was about 16,000 gauss.

The source of light.—An image of the tungsten bead of a powerful point-o-lite lamp was focussed on the slit of a constant deviation spectrograph, which was used as a monochromator. A slit of width less than one mm. selected out various regions of the spectrum. The spectral band coming through the slit was not more than 50 Å. in the green and blue regions and was about 100 Å. in the red and yellow regions. The mean wavelength of the band was determined with a calibrated direct vision spectroscope. For accurate monochromatisation a mercury point-o-lite or a sodium lamp was substituted for the tungsten lamp. Since a monochromator with a single prism was used, the scattered light gave a continuous background. This was not considerable when the brighter regions of the spectrum, *i.e.*, from 6000 Å. to 4800 Å. are used, but became a serious source of error for wavelengths below 4800 Å. The magnetic rotation of diamond was therefore studied only over a range of wavelengths between 6000 Å. and 4800 Å. where the background intensity did not affect the observations. On certain occasions the monochromator was dispensed with, and sodium or mercury lamps with adequate filters were used.

Two wide-angled nicols giving perfect extinction were used as polariser and analyser respectively. The rotation of the analysing nicol was measured with a lamp and scale, the scale being at 80 cms. from the mirror. The diamond plate was introduced between the pole pieces in a wooden holder and care was taken to see that the crystal was not strained thereby introducing birefringence. The surface of the diamond was kept normal to the incident light, as otherwise, there would be a rotation of the plane of polarisation due to refraction at oblique incidence. Although this scarcely affected the Faraday effect, it was more convenient to avoid such rotation.

The general procedure of the experiment was as follows. The light of the necessary wavelength was focussed on the slit and the diamond introduced in position and the nicols then accurately crossed. A large number of readings (usually 25) were taken for this crossed position. It was found that settings could be made within 1·5 mm. when the scale was at 80 cms. distance. The mean of these readings was taken as the position of extinction. The magnetic field was then put on by passing a current of 6 amps. through the coils and the nicols crossed again. The mean of 25 readings gave the

position of extinction. Similarly, the extinction position when the field was reversed was found. The rotation of the plane of polarisation was calculated by taking half the difference between the two extinction positions, the zero-reading acting as a check on the accuracy of measurement.

Half-shades and other appliances for finding out the exact extinction position could not be successfully used in the case of diamond. One seldom obtained complete extinction in all the regions of the diamond when it was observed between crossed nicols. To get the correct extinction position it was, therefore, necessary to view only those regions which gave total extinction. The half shade gave the mean extinction position for the whole plate of diamond and hence gave less accurate results than when ordinary nicols were used. In fact when a half-shade was used, rotations of the same order as those observed with nicols were obtained, but the differences between individual readings were larger and hence the method was untrustworthy. The numerous concordant values obtained when nicols were used bore testimony to the accuracy of this method.

The absolute value of the Verdet's constant of diamond was determined by comparing the rotation produced by it with that produced by a thin crystal of rock salt placed exactly in the same position as the diamond. This procedure was adopted so that if there was a minute rotation due to the effect of the magnetic field on the nicols, the cover slips protecting the nicols and other optical parts, the same could be eliminated. Separate measurements of these spurious effects were made and they were found to be less than 5% of the rotation produced by diamond. From the knowledge of the magnetic rotation due to a crystal of rock salt of known thickness and of the accurate Verdet's constant for it (from the International Critical Tables), it is possible to calculate the effective field. Table I gives the effective fields calculated from the rotation by substances of different thicknesses. The standard values of the Verdet's constant for these substances for the sodium 5890 line which were used for the calculation of the field are also given. The value obtained with a search coil (0·7 cm. long) is also given. These measurements were carried out for two different field strengths which were used in the determination of the magneto-optic rotation. The value of the field appears lower when the thickness of the substance used is small. This is, as already mentioned, due to the rotation produced (in the opposite direction) by the effect of the magnetic field on the optical system. At the foot of the table has been entered the ratio of the Verdet's constant for water for the wavelengths 5890 Å. and 5460 Å. observed experimentally by the present writer and that given in the International Critical Tables.

The two values agree quite closely, indicating the accuracy with which the settings could be made.

TABLE I

Verdet's constant at 25°C. for 5890A.

NaCl .. 0·03585 mins. per cm. per gauss.

Water .. 0.01306 „ „

A. Distance between pole pieces, 0·95 cms.
Distance of scale from mirror, 79 cms.

Substance	Thickness in cm.	Wavelength in Å. U.	Rotation in cms.	Rotation in mins.	Field in gauss
NaCl ..	0·046	5890	1·24	27·54	16700
	0·098	„	2·66	59·1	16820
	0·417	„	11·4	254·3	17010
Water ..	0·105	„	1·03	23·0	16720
	0·372	„	3·70	82·6	17010

Field determined with search coil 17100 gauss.

B. Distance between pole pieces, 1·05 cms.
Distance of scale from mirror, 81·7 cms.

Substance	Thickness in cm.	Wavelength in Å. U.	Rotation in cms.	Rotation in mins.	Field in gauss
NaCl ..	0·043	5890	1·16	24·4	15810
	0·093	„	2·57	54·0	15880
	0·401	„	10·85	227·8	15890
Water ..	0·372	5890	3·37	70·8	15860
	0·372	5460	3·96	83·6	15880

$\frac{V_{5460}}{V_{5890}}$ for water at 25° 1·184 (I. C. T.)

„ „ „ 1·175 (Observed)

3. OBSERVATIONAL DATA

The cleavage plate N.C. 157 was used for the study of the variations of the Verdet's constant with wavelength. Table II gives the Verdet's constant obtained for different wavelengths between 6000 Å. and 4800 Å. The last column in the table gives the magneto-optic anamoly, the method of calculation of which is indicated later. Two monochromatic wavelengths 5890 Å. (sodium) and 5460 Å. (mercury) were used in the measurement of the Verdet's constant in N.C. 177. The values are given in Table III, each of them being a mean of 100 readings. The ratio $\frac{V_{5460}}{V_{5890}} = 1·191$ and the ratio calculated from the Becquerel formula is 1·179. Table IV gives the results

obtained with N.C. 73 and N.C. 4 and also those obtained for a combination of N.C. 157 and N.C. 73.

TABLE II

N. C. 157. Thickness of the plate 0·58 mm.
Distance between pole pieces 0·95 cm. Effective field 16700 gauss.
Distance of scale from mirror, 79 cms.

Wavelength in Å. U.	Rotation in cms.	Rotation in mins.	Verdet's constant in mins per cm. per gauss	γ
5890	0·97	22·3	0·0230	27·4
5800	1·00	23·0	0·0237	28·1
5600	1·07	24·6	0·0254	27·9
5400	1·20	27·6	0·0285	28·9
5200	1·27	29·3	0·0302	28·2
5025	1·35	31·1	0·0321	27·8
4860	1·41	32·4	0·0335	26·9

TABLE III

N. C. 177. Thickness of the plate 0·85 mm. Effective field 15800 gauss.
Distance of the scale from the mirror, 81·7 cms.

Wavelength in Å. U.	Rotation in cms.	Rotation in mins.	Verdet's constant mins. per cm per gauss	γ
5890 (*Na*) ..	1·36	31·3	0·0233	27·6
5461 (Hg) ..	1·62	37·3	0·0278	27·9

$$\frac{V_{5460}}{V_{5890}} = 1{\cdot}191 \text{ (experimental)}$$
$$= 1{\cdot}179 \text{ (from Becquerel's formula)}$$

TABLE IV

Effective field 16700 *gauss. Distance of scale from mirror,* 79 *cms.*

Diamond	Thickness in mms.	Wavelength in Å. U.	Rotation in cms.	Verdet's constant	γ
N. C. 73 ..	0·68	5800	1·20	0·0243	28·9
		5400	1·35	0·0273	27·5
		5025	1·54	0·0312	26·9
N. C. 73 and N. C. 157	1·26	5800	2·22	0·0243	28·9
		5400	2·67	0·0292	29·6
N. C. 4 (Crystal) ..	4·8	5800	7·44	0·0209	25·4
		5400	9·08	0·0256	25·6

As already remarked, the result obtained with the crystal N.C. 4 is not so trustworthy as that obtained with the cleavage plates.

4. The Magneto-Optic Constants of Diamond

The value of γ was determined in the following way, Peter (1923) determined the refractive index of diamond from 6790 Å. to 2265 Å. and found the refractive index in this region to be well expressed by the formula

$$n^2 - 1 = \frac{\epsilon_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{\epsilon_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

where $\epsilon_1 = 0{\cdot}3306$ $\lambda_1 = 1750$ Å.

$\epsilon_2 = 4{\cdot}3356$ $\lambda_2 = 1060$ Å.

From this formula $\lambda \frac{dn}{d\lambda}$ was calculated for those wavelengths for which the magneto-optic rotation has been determined. Using the relation

$$V = \gamma \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}$$

γ was found and is expressed as a percentage. γ is thus the percentage ratio of the observed magnetic rotation to that calculated from the unmodified Becquerel formula. The last columns of each of the Tables II, III and IV give the value of γ for the wavelengths indicated. It may be noticed that for a range of wavelengths from 6000 Å. to 4800 Å., the value of γ is, within the limits of experimental error, constant.

From the examination of the above results, the following can be taken as the standard values of the various magneto-optic constants for diamond.

Verdet's constant 5890 Å .. 0·0233 mins. per cm. per gauss

5460 Å .. 0·0278 ,, ,,

$\frac{V_{5460}}{V_{5890}}$ = 1·191 (observed)

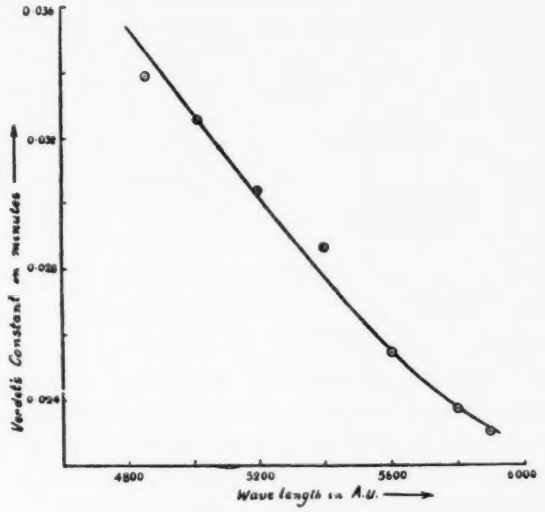
= 1·179 (calculated from the Becquerel formula)

The mean value of γ for the visible spectrum = 27·8.

Fig. 1 gives the experimental values of the magnetic rotation for various wavelengths, as also the theoretical values, calculated from the Becquerel formula with $\gamma = 28\%$. It is estimated that in the measurement of the magnetic rotation, an error of not more than 4% could have crept in.

5. The Magneto-Optic Constants of Zinc Blende

Since sphalerite (ZnS) has a crystal structure similar to that of diamond it was considered worthwhile to determine its Verdet's constant and the magneto-optic anamoly. Using the same arrangement as that described for



—— Theoretical curve from Becquerel's formula ($\gamma = 28\%$)

⊙ Experimental points (N.C. 157)

FIG. 1. Observed and Calculated Faraday Rotations of Diamond.

diamond, the magnetic rotation for a beautiful transparent plate of sphalerite in the possession of Sir C. V. Raman was determined for different wavelengths. Using the refractive index data of Maria Mell (1923) the magneto-optic anamoly for these wavelengths was determined. The results are tabulated in Table V. Table VI compares the results obtained by the present writer with those obtained by different authors. The agreement between these results is quite satisfactory.

TABLE V

Sphalerite (ZnS). Effective field, 16700 gauss. Thickness of the specimen, 5·55 mm.

Wavelength in Å. U.	Rotation in degrees	Verdet's Constant	γ %
6100 ..	32·7	0·211	91
5890 (Na) ..	35·0	0·226	91
5780 (Hg) ..	38·1	0·246	90
5600 ..	40·4	0·261	90
5460 (Hg) ..	44·5	0·287	92
5400 ..	45·6	0·294	92
5200 ..	52·4	0·333	91·5
4360 (Hg) ..	90·25	0·582	91

TABLE VI

Sphalerite (ZnS)

Constant	Author	Other observers
Verdet's constant		
5890 A ..	0·226	0·225 (Becquerel) 1877
5460 A ..	0·287	0·286 (Cotton) 1932
$\frac{V_{4360}}{V_{5460}}$ ..	2·03	2·057 (,,)
$\frac{V_{5780}}{V_{5460}}$ ..	0·852	0·863 (,,)

6. DISCUSSION OF RESULTS

Table VII gives the optical and the magneto-optic constants of some cubic crystals of relatively simple structure. The magneto-optic anamoly γ for all these crystals is constant over the range of the visible spectrum.

TABLE VII

Substance	Refractive Index 5890 Å	Dispersion 5890 Å	Verdet's constant 5890 Å	γ %
ZnS ..	2·3683	4611	0·226	91
NaCl ..	1·5443	669	0·03585	85
KCl ..	1·4904	586	0·02858	75
CaF_2 ..	1·4338	242	0·00883	66
Diamond ..	2·4172	1298	0·0233	28

This indicates that the electrons which give rise to dispersion are also those responsible for the magneto-optic rotation. The value of γ for atoms and ions having the inert gas configuration has been shown (Van Vleck, 1932) to be 100%, *i.e.*, they obey the unmodified Becquerel formula. Hence we may legitimately infer that a deviation of γ from this value is an indication of the extent to which the electron configuration departs from the inert-gas state. The low value of γ in the case of diamond finds a natural explanation on this basis. The four electrons in the carbon atom are shared between the neighbouring atom and the electronic configuration is considerably different from that of the inert gas. Rock salt and sylvine are usually considered to be typical examples of crystals with ionic binding. In that case except for the slight perturbation produced by the crystal field, the sodium and chlorine ions in rock salt have the inert-gas structure and hence should have a value for γ approximating to 100%. Actually, as we see in Table VII the value of γ for these crystals is considerably less. This can only mean

that the alkali and halogen structures in these alkali halides deviate from the inert-gas configuration by a considerable extent. It seems possible that the binding between them may be at least partly covalent in nature. This is even clearer in the case of CaF_2. On this view, the fact that the value of γ for ZnS approaches that for an inert-gas configuration is significant. It indicates that the binding between Zn and S is much nearer being an electrovalent than of a covalent nature, in spite of the geometrical structure of the crystal being similar to that of diamond. Incidentally it may be remarked that in agreement with this view, ZnS is a strongly piezo-electric crystal.

In conclusion the author wishes to record his deep sense of gratitude to Professor Sir C. V. Raman, for his helpful interest and encouragement in this work.

7. Summary

With three thin cleavage plates and a natural crystal of diamond, all of which had an almost negligible birefringence, the magnitude of the Faraday rotation was measured for a series of different wavelengths in the visible spectrum. The magnetic rotation was proportional to the dispersion and the Verdet's constant for the wavelengths 5890 Å. and 5460 Å. were 0·0233 and 0·0278 minutes per cm. per gauss respectively. The magnetic rotation followed the modified Becquerel formula with the multiplying factor γ, which remains sensibly constant in the visible region, equal to 28%. The value of this constant is much less than that for most carbon compounds available as liquids for which it is known. The magneto-optic constants for sphalerite (ZnS) were also determined and it was found that γ, in this case, was 91%. The significance of these results is discussed.

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THE CLEAVAGE PROPERTIES OF DIAMOND

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1. Introduction

The easy and perfect cleavage of diamond along the (111) plane has long been known to the Indian lapidaries. Cleavage plates of large area polished and slightly facetted at the edges were extensively used in jewellery, but this form of adornment has in recent years gone out of fashion. In consequence, such plates can be purchased from the jewellers in the larger cities of India. Sir C. V. Raman has in his collection several of these plates and they have proved extremely useful in the study of the different properties of diamond. During his investigation of the X-ray topographs of diamond, Mr. G. N. Ramachandran examined this material and found that three out of the fifty plates studied had a (211) cleavage. Sutton (1928) in his book on the South African diamonds remarks that while the (111) cleavage is most common, the (110) is also occasionally found.

In view of the facts stated above, it appeared desirable to undertake a systematic investigation of the cleavage properties of diamond. A calculation of the cleavage energy of various planes in diamond indicated the possibility of numerous other cleavages besides those mentioned above. A careful goniometric study of 15 crystal fragments in Sir C. V. Raman's collection was accordingly made which resulted in a striking confirmation of this idea. The paper records the results of these studies.

2. The Nature of Cleavage

"Cleavage is not merely a tendency to fracture with the production of two more or less plane fracture surfaces along an approximately definite direction. It is the facility for splitting along an absolutely *true* plane having an orientation within the crystal definitely fixed within one or two minutes of arc" (Tutton). The (111) cleavage of diamond is a striking example of the above definition. Many writers (1932) have tried to give an explanation for the presence of the (111) cleavage. One set of authors attribute the perfection of the cleavage to the fact that the spacing is a maximum for the (111) planes, while others suggest that it is because the surface energy

is minimum for the (111) plane. A calculation of the surface energies of different planes shows that this is indeed the case, but this energy is not greatly different from that for the other nearby planes. Bearing in mind the fact that in the crude method used for cleaving diamonds the energies employed may be much in excess of what is required to effect cleavage in any direction, one would expect to have a fracture rather than a perfect cleavage. From these facts it would seem that considerations of surface energy alone are not sufficient to explain the "atomic accuracy" of the (111) cleavage.

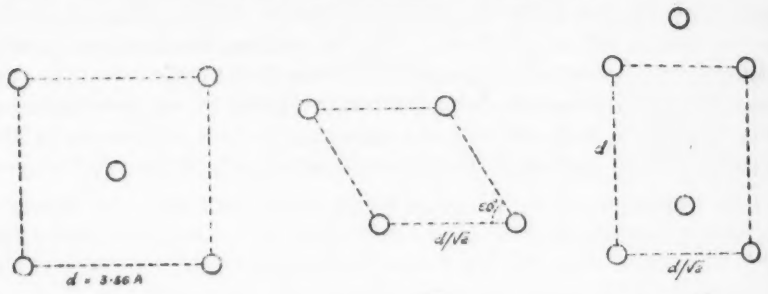
An inspection of the diamond model shows that the (111) planes are not equally spaced, the ratio of the distances between alternate planes being 1:3. It is also found that the number of bonds cut per unit area depends on the place at which the two parts of the crystal are separated. If cleavage is effected between the two octahedral layers which are farther apart, then one bond per atom will have to be cut. On the other hand, if diamond is cleaved between the octahedral layers that are closer together, three bonds per atom will have to be ruptured. It is, therefore, obvious that a cleavage in the former position requires only a third as much energy as for one in the latter position. If, therefore, a cleavage starts parallel to the (111) plane between two layers which are farther apart, it will continue in the same plane since any slight deviation in the direction would involve a threefold increase in energy. This sudden increase in energy which accompanies any deviations appears to be responsible for maintaining the (111) cleavage along a true geometric plane.

3. The Calculation of the Energy of Cleavage

It is reasonable to assume that the energy required to cleave a diamond along a particular plane is equal to that required to rupture the bonds connecting atoms situated on either side of the plane. The number of bonds cut per unit area thus gives a measure of the energy of cleavage for a particular plane. Harkins (1942) has used this idea to calculate the surface energy of the (111) and (100) planes. Since two surfaces are formed by cleavage, the surface energy should be equal to half the cleavage energy. In this section we shall calculate the cleavage energy of a few planes in diamond.

In the case of simpler planes such as (100), (111) and (110), the calculations can be made in a very simple manner. In Fig. 1 *a*, the area bounded by dotted lines represents the repetitive unit cell in the (100) plane which is a square whose side is $d = 3{\cdot}56$ Å, the length of the unit cubic cell in the diamond lattice. There are two atoms per unit cell (one at the corner and one at the centre) so that the number of atoms per unit area is $2/d^2$. As

two bonds connect each atom with the atoms in the neighbouring plane, the number of bonds ruptured per unit area is $n_{100} = 4/d^2$.



(a) (b) (c)

FIG. 1

For the (111) plane the unit cell is a rhombus of side $d/\sqrt{2}$ and angle 60° which is shown in Fig. 1 *b*. There is only one atom per unit cell whose area is $d^2\sqrt{3}/4$. One bond connects each atom with an atom in the upper layer, while three connect it with atoms in the lower layer. The number of bonds cut per unit area n_{111} is therefore, $4/d^2\sqrt{3}$ or $4\sqrt{3}/d^2$ according as the cleavage is above or below the plane under consideration.

The unit cell in the case of (110) is shown in Fig. 1 *c*. It is a rectangle of sides d and $d/\sqrt{2}$ containing two atoms. Since each atom in this plane

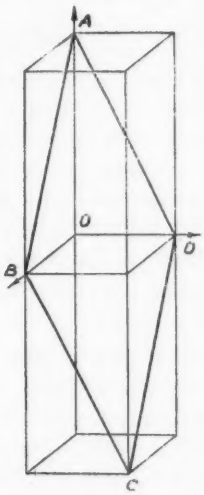


FIG. 2

is connected by one bond to an atom in the neighbouring plane, the number of bonds cut per unit area n_{110} is $2\sqrt{2}/d^2$.

For more complicated planes the following general analytical method is adopted. Considering the (*hkl*) plane, let H, K and L be the corresponding indices in the Weiss notation (*i.e.*, H, K and L are the smallest integral intercepts made by the plane on the co-ordinate axes). In Fig. 2 the unit cell in the (*hkl*) plane is represented by the parallelogram ABCD the area of which can be calculated from the condition OB = H*d*, OD = K*d*, and OA = L*d*. The equation to this plane is

$$hx + ky + lz - p = 0$$

where $p = h\mathrm{H} = k\mathrm{K} = l\mathrm{L}$. If the co-ordinates of an atom are substituted in the expression on the left hand side, the sign of the quantity obtained indicates the position of the atom with respect to the plane. The atom lies on the same or the opposite side of the plane as the origin according as the sign is negative or positive. Having thus found out the position of all the atoms in the diamond structure with respect to the plane (*hkl*), the number of bonds which connect atoms on opposite sides of the plane can be counted. A difficulty arises when an atom lies on a plane. In this case the plane of separation is slightly shifted away from or towards the origin and the number of bonds cut is counted in either case. The two may either be equal or different. If different the lower value is taken to calculate the cleavage energy. As an example we shall take the (221) plane. Here OB = *d*, OD = *d* and OA = 2*d* and the area of the cell is $3d^2$. It is found that the number of bonds cut per unit cell is 8 or 12 according as the cleavage takes place in the positive or the negative side of the plane ABCD. Consequently $n_{221} = 8/3d^2$. Similar calculations have been made for other planes.

The energy required to rupture a C–C bond has been calculated from thermo-chemical consideration to be $6{\cdot}22 \times 10^{-12}$ ergs. (Harkins, *loc.cit.*). Accepting this value the cleavage energy of various planes have been determined. The results are tabulated in Table I with the planes arranged in order of increasing energy. It is found that the number of bonds cut per unit area can be given by the expression

$$n_{hkl} = \frac{4}{d^2}\frac{h}{\sqrt{h^2 + k^2 + l^2}}$$

where *h* is the largest of the three indices.

A study of Table I shows that the energy of the (111) plane is the least and is an absolute minimum. The (111) plane must, therefore, be a plane

of easy cleavage. The energy of the (100) plane is the largest and is about 80% higher than that for the (111) planes and the other planes have energies intermediate between these. As has been mentioned above, the (110) and the (112) cleavages have been observed in diamond. Table I shows that there are planes having energies less than these, and it is quite probable that

TABLE I

Plane	Angle between plane and the (111) plane	Expression for No. of bonds cut per $(3{\cdot}56\ \text{Å})^2$	$\frac{h}{\sqrt{h^2+k^2+l^2}}$	Cleavage energy in ergs per cm^2
111	0°	$4/\sqrt{3}$	$1/\sqrt{3}$	11330
332	10° 0′	$12/\sqrt{22}$	$3/\sqrt{22}$	12550
221	15° 48′	8/3	2/3	13080
331	22° 0′	$12/\sqrt{19}$	$3/\sqrt{19}$	13510
110	35° 16′	$4/\sqrt{2}$	$1/\sqrt{2}$	13880
322	11° 24′	$12/\sqrt{17}$	$3/\sqrt{17}$	14290
321	22° 12′	$12/\sqrt{14}$	$3/\sqrt{14}$	15730
211	19° 28′	$8/\sqrt{6}$	$2/\sqrt{6}$	16030
320	36° 48′	$12/\sqrt{13}$	$3/\sqrt{13}$	16330
210	39° 14′	$8/\sqrt{5}$	$2/\sqrt{5}$	17560
311	29° 30′	$12/\sqrt{11}$	$3/\sqrt{11}$	17750
100	54° 44′	4	1	19630

cleavages parallel to these might also occur under proper conditions. One should expect the relative abundance of the cleavage planes to follow the order listed in Table I, (111) being most frequent and (100) being almost absent. From the general expression for the cleavage energy given above, it can be shown that the cleavage energy diminishes as the plane is tilted progressively towards a (111) plane. Consequently, curved cleavages or fractures could also be expected to occur in diamond. If these curved fractures attain directions near about an octahedral plane, they might actually coincide with it and become plane cleavages.

4. METHODS OF STUDY

To verify the deductions from theory, a systematic study of 15 fragments of diamond in Sir C. V. Raman's collection was made. A visual examination with a pocket lens of these fragments revealed that most of them contained the usual (111) cleavages, but 9 of them appeared to have cleavages

other than the (111). Each of these nine was used for careful goniometric study, and it was found that while four crystals had planes other than the octahedral, the rest had very interesting fractures which were irregular and more or less curved. A Mier's student goniometer with a collimator and telescope attachment capable of reading upto 1 minute of arc was used. The crystal was attached to the instrument with soft wax and all adjustments of the crystal were made by hand. The angles between the cleavage faces were measured with an accuracy not greater than 15 minutes of arc, but these were quite sufficient to identify the different planes. The octahedral cleavages were very easy to recognise from the perfection and splendent lusture they exhibited. While these planes gave extremely sharp signals in the telescope, the other planes did not give such sharp ones. Only the angles between those surfaces which gave good signals were measured. Care was always taken to see that curved surfaces were not used for observation. When a low-power microscope was focussed on the diamond and the milled head of the goniometer rotated, reflections from the plane faces flashed into the microscope and they did not remain in the field of view for a rotation of more than 15 minutes of arc. In the case of curved planes or faces, the reflection remained in the field of view even when the head was rotated through 2°. It must also be mentioned that reflections from curved faces were extremely feeble and diffuse when observed with a telescope and could easily be distinguished from the reflection from plane faces.

5. Observational Data

N.C. 42 had three large cleavage faces which were octahedral. Two of these were absolutely plane. The third showed the existence of two or three other cleavage faces. They lay in the [110] zone and measurement showed that two of them were (221) faces. The third which gave a feeble but sharp signal was near about the (332). There were also some curved fracture faces on the surfaces of the crystal.

N.C. 59 was a crystal fragment with a large number of cleavage faces on its surface. The specimen is one of the collection of diamonds presented to Sir C. V. Raman by the De Beers Corporation of Kimberley. In one of the [110] zones the following planes were identified: 4 beautiful (111) planes, one (331), one (110), one (322) and one (211). In another perpendicular zone, two (111), one (221), one (331), one (110) and one (322) were found. Although all the planes were quite small, the signals obtained from (111), (221), (110) and (322) were extremely sharp. One octahedral face which appeared to be very drusy was found on examination, to consist of hundreds of tiny (111) planes. In a third zone, one (111) and a tiny (322)

plane were found. There were also some curved faces on the diamond, and some of the curved faces ended as tiny flat (111) cleavage faces.

N.C. 45 was a natural crystal which had been broken on one side. Three large prominent cleavage planes are visible on its surface. Two of them were (111) and the third a (110) plane. There was also another tiny (110) plane on the crystal. The large (110) surface had large striations, which mainly consisted of fine (221) planes arranged in a step-like order.

N.C. 174 was a thick flat polished plate with a few cleavage faces on the girdle. Four of these were octahedral cleavages. One (331), one (110), one (221) and a tiny (332) were also found. The angles between the two large faces of the plate and the planes of known indices in the girdle were measured and it was found that the flat face was approximately a (431) plane. In view of the fact that the surface is polished and the plate is quite thick, it is impossible to say whether the two flat faces are cleavage planes or not. The other crystals examined had the (111) cleavage and also irregular and curved fractures. N.C. 194 was a rectangular cleavage plate, all its six faces being perfect octahedral cleavages. N.C. 49 had a large octahedral cleavage followed by a curved face with fine striations. N.C. 39 was a yellowish crystal with two (111) faces and a fracture containing a large number of tiny octahedral faces. N.C. 32 was a black diamond with two large (111) faces and with several tiny curved faces. N.C. 50 had a good many cleavage faces and many of them were curved.

Table II gives the collection of the results obtained. The numbers in the vertical columns indicate the number of independent planes of a specific

TABLE II

Diamond Planes	N.C. 42	N.C. 59	N.C. 45	N.C. 174	N.C. 49	N.C. 39	N.C. 32	N.C. 50	N.C. 194
111	3*l*	6*l*	1*l* 1*l*	4*l*	2*l*	3*l*	2*l*	3*l*	6*l*
332	1*l*			1*l*					
221	1*s*	2*m*	1*s*	1*s*					
331		2*s*		1*s*					
110		2*m*	1*l* 1*l*						
322		3*s*							
211		2*s*							

index on a particular diamond. All the planes which gave a common signal at a particular setting have been taken together and counted as one. The letters accompanying each number indicate the size of the planes. *l* (large) signifies planes having an area greater than two sq. mm., *m* (medium) those with areas between one and two sq. mm., *s* (small) those with areas between a half and one sq. mm., while *t* (tiny) those with areas less than half a sq. mm.

Table II can in no way be said to represent the relative abundance of different cleavages, as the number of cases examined has been too few. Even so, an idea of the relative frequencies of different planes can be obtained from the table. The planes have been arranged in order of increasing energy and one could see that the lesser the energy of a plane the more frequent is its occurrence. It may be mentioned here that amongst the planes of cleavage listed above, (111), (221), (331) and (322) belong to the category in which the distance between alternate layers of atoms are not equal.

In conclusion, the author wishes to express his thanks to Sir C. V. Raman for his encouragement and interest in this investigation.

Summary

Calculations of the cleavage energies of various planes in diamond indicated the presence of cleavages other than those already known. A careful goniometric study of several crystal fragments in Sir C. V. Raman's collection revealed numerous other cleavages. The presence of the following cleavage has been definitely established: (111), (221), (110), (322), (331), (211) and (332). The (111) cleavage was found to be by far the most perfect and most abundant, while (221) and (110) cleavages were not uncommon. It is suggested that the perfection of the (111) cleavage is not merely because that plane has the minimum cleavage energy but also due to the fact that on either side of the plane of easy cleavage lie layers of atoms having three times the cleavage energy. It was also found that diamond definitely has curved fractures and the theory developed in the earlier part of the paper accounts for the existence of these.

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A THEORY OF THE CRYSTAL FORMS OF DIAMOND

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1. Introduction

The number of different kinds of planes permitted by the law of rational indices to appear as faces on a crystal is practically unlimited. The number of "forms" actually observed, however, is limited and there is a decided preference for a few amongst them. This is one of the most striking facts of geometric crystallography and its explanation is obviously of importance. Pierre Curie (1885) stressed the role played by the surface energy of the faces in determining the "forms" of the crystal. According to him, the different faces of a crystal have different surface energies and the form of the crystal as a whole is determined by the condition that the total surface energy of the crystal should be a minimum. According to W. Gibbs (1877), on the other hand, it is the velocity of growth in different directions which is the determining factor, while the surface energy of the crystal plays a subordinate role and is only effective in the case of crystals of submicroscopic size.

We have little direct knowledge as to how diamond is actually formed in nature. It is necessary, therefore, to rely upon the indications furnished by the observed forms of the crystals. One of the most remarkable facts about diamond is the curvature of the faces which is a very common and strongly marked feature. This is particularly noticeable in the case of the diamonds found in the State of Panna in Central India. Writing after a visit during which he had the opportunity of examining several hundreds of specimens, Sir C. V. Raman (1942) drew attention to the remarkable beauty of the Panna crystals with their exquisitely perfect geometric forms, their smooth lustrous surfaces and the sharpness of the edges which divide the curved faces into distinct sections. Basing himself on the characters exhibited by the Panna diamonds, he outlined a theory of the crystal forms of diamond which may be usefully quoted here *in extenso*.

"I wish to put forward tentatively a suggestion which seems to me to offer a reasonable interpretation of the facts stated above. If carbon liquefied under suitable conditions of temperature and pressure when surrounded by molten silicious material, the form of the drops of the liquid diamond

would be determined by the interfacial tension and would be spherical, provided the valence bonds between the atoms of carbon in the liquid were oriented completely at random. If, however, some measure of regularity in the orientation of the valence bonds could be assumed, the conditions within the liquid would roughly approximate to those in the solid crystal; in other words, *diamond in the molten state would be a liquid crystal.* The interfacial tension would then vary with direction and the surfaces of minimum energy would not be spherical but would tend to show some resemblance to the forms exhibited by a cubic crystal. If the shapes assumed by diamond in the liquid crystalline state persisted on solidification or else suffered only minor changes, we would have an explanation of the forms now observed."

The ideas expressed in the foregoing quotation have been made use of in the introductory paper of this symposium (Raman and Ramaseshan,

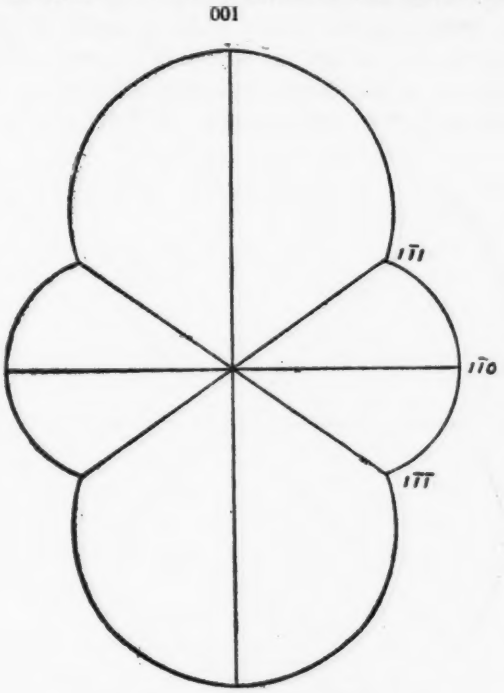

FIG. 1. Surface Energies in the [110] zone

1946) in connection with the scheme of classification of the crystal forms of diamond adopted in that paper. In the present paper, the same ideas are

developed further and given a semi-quantitative form. For this purpose, the calculation of the surface energy of the various crystallographic planes in diamond made by the present writer for a different purpose (Ramaseshan, 1946) are utilised. The theory succeeds in explaining some of the principal facts which emerge from a study of the crystal forms.

2. Surface Energies of the Crystal Planes

The surface energy of the different crystallographic planes in diamond is very large, being at least ten times as great as the surface tension of mercury at ordinary temperatures. Hence, the surface tension may be expected to play a notable part in shaping the crystals of diamond under the conditions of their formation. For a proper approach to the subject, it is necessary to evaluate the surface energy for numerous planes lying in different zones. This has been already done by the present author in the paper on the cleavage properties of diamond appearing in the present symposium (Ramaseshan, 1946), and we may use the results here, taking the surface energy per unit area to be half the energy of cleavage. In Figs. 1, 2 and 3 the surface energies of the various crystallographic planes in the [110], [100] and [111] zones have been represented in the form of polar diagrams.

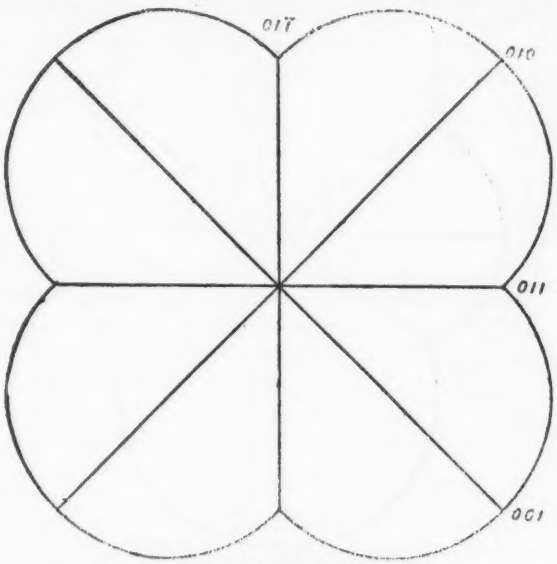

Fig. 2. Surface Energies in the [100] zone

The following points emerge from a scrutiny of the figures. The surface energy is an absolute minimum for the (111) planes, and an absolute maximum

for the (100) planes; in the [110] zone the surface energy is a minimum for the (111) planes and a maximum for the (100) planes, while there is an intermediate maximum for the (110) planes; in the [100] zone, the surface energy is a minimum for the (110) planes and a maximum for the (100) planes; in the [111] zone, the surface energy is a minimum for the (110) planes and a maximum for the (211) planes. The situation thus described enables us at least qualitatively to understand the following empirically known facts:

(1) The plane faces which have been noticed to occur in diamond either by themselves or in combination with curved forms are, in the great majority of cases, if not in all, the (111) planes.

(2) Curved forms *approximately* parallel to either to the (111) or the (110) planes are a common feature in diamond.

(3) Curved forms parallel to the (100) planes are rarely, if ever, observed.

(4) Many diamonds exhibit forms which may be *approximately* described as a combination of the (111) and (110) forms, these however exhibiting a marked curvature.

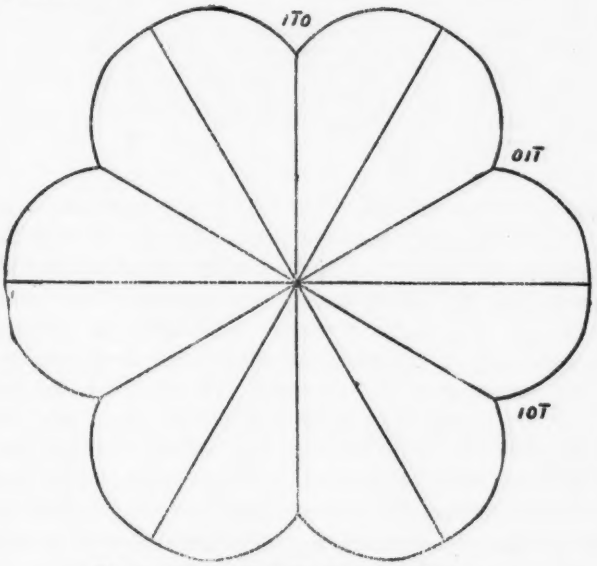

FIG. 3. Surface Energies in the [111] zone

3. THE AGGREGATE SURFACE ENERGY

According to P. Curie (*loc. cit.*), it is the total surface energy of the crystal that plays the determining role in respect of the forms assumed by

it. In the case of diamond, this would have to be found by integration over the curved areas and by addition of the surface energies of the plane areas (if any) appearing in combination with them. It is not without interest, however, to consider the purely hypothetical cases of the various regular forms, bounded by plane faces all of the same kind and to evaluate the surface energy of each of these. It then becomes evident that forms which present faces with a relatively small surface energy may nevertheless have greater aggregate energies by reason of their presenting a larger area for the same volume.

TABLE I

I	II	III	IV	V
Plane	Surface energy per unit area	Description	$\frac{\text{Area}}{(\text{Volume})^{2/3}}$	Product of II and IV
111	5665	Octahedron	5·718	32390
		Tetrahedron	7·204	40810
221	6545	Tris-octahedron	5·26	34430
		Tris-tetrahedron	5·793	37910
110	6945	Dodecahedron	5·346	37130
321	7870	Hexakis-octahedron	5·009	39430
		Hexakis-tetrahedron	5·395	42460
210	8780	Tetrakis-hexahedron	5·119	44940
100	9815	Cube	6	58890

The figures set out in Table I furnish us with some useful pointers. If, for instance, we were concerned with forms of diamond exhibiting full octahedral symmetry, the simple octahedron with eight faces would be a more probable form than the others having that symmetry but exhibiting 24 or 48 faces. On the other hand, if we are concerned with diamond having a tetrahedral symmetry of structure, its appearance in the forms specifically exhibiting that symmetry is not favoured. In particular, the appearance of the form of the simple tetrahedron would be much less probable than that of the rhombic dodecahedron which is common to both the tetrahedral and octahedral symmetry classes. It is also noticed that the appearance of the other forms common to the two symmetry classes, *viz.*, the tetrakis-hexahedron and the cube, is much less probable than that of the dodecahedron. Similar considerations may also be applied to find the likelihood of appearance of various interpenetration forms. It is readily shown, for instance, that the Haidinger diamond or one similar thereto would have a surface energy for any given volume only slightly greater than that of a simple octahedron and hence that its appearance would be favoured.

4. Relation of Curvature to Surface Energy

A liquid drop composed of isotropic material would naturally assume the shape of a sphere. Whether a liquid with anisotropic structure would show a similar behaviour depends on whether its surface energy is independent of orientation or not. In the particular case of molten carbon, it would seem that a variation of surface energy with orientation is very probable and hence the liquid would tend to take up a configuration different from that of a sphere. There would be clearly two opposing effects; areas having a smaller tension would tend to enlarge at the expense of areas having a greater, thereby diminishing the total energy, while on the other hand, the pressure within the drop would cause areas with a smaller tension to become more strongly curved, thereby diminishing their extent. What the resulting configuration would be is a problem—and not a simple one—in the calculus of variations.

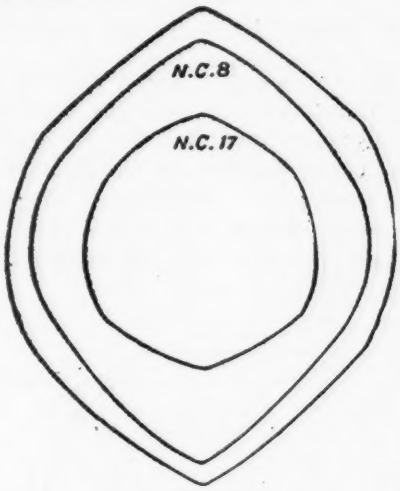

Fig. 4. Form of N.C. 2, N.C. 8 and N.C. 17 in the [110] zone

For our present purpose, it is sufficient to draw attention to the obvious correlations which exist between the surface energy diagrams reproduced as Figs. 1, 2 and 3 above with the observed forms of diamond in the respective zones. For this purpose, the outlines of three diamonds in the collection, N.C. 2, N.C. 8 and N.C. 17 of progressively diminishing size and having a fairly symmetrical shape have been photographically recorded for these zones. The outlines have been reproduced inside each other in Figs. 4, 5 and 6 respectively in the same zones.

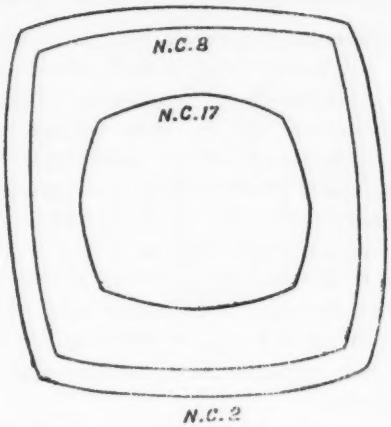

FIG. 5. Form of N.C. 2, N.C. 8 and N.C. 17 in the [100] zone

Comparisons of Fig. 4 with Fig. 1, Fig. 5 with Fig. 2 and Fig. 6 with Fig. 3 are instructive. In each case, the following features are noticed. The smaller the diamond, the more marked is the curvature of its faces. At the same time, the outlines of the form for the diamonds of different sizes tend to run parallel to each other. The areas in the vicinity of the triad axis in the [110] zone are the flattest, while in the vicinity of the dyad axes, the surfaces present sharp edges; in the (110) directions, there is a marked curvature.

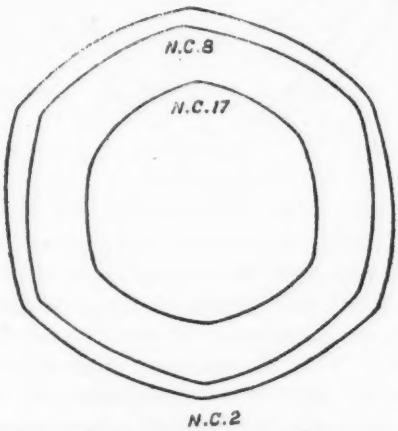

FIG. 6. Form of N.C. 2, N.C. 8 and N.C. 17 in the [111] zone

In the [100] zone, the surface exhibits a relatively small curvature in the (110) directions and others adjacent to it, while in the (100) direction, the surface presents sharp edges. In the [111] zone, the curvature is throughout very marked, but there are distinct kinks in the (112) directions, *viz.*, those normal to which the surface tension is greatest in that zone.

In conclusion, the author wishes to thank Sir C. V. Raman for his kind interest and useful discussions.

5. Summary

The calculations of the energies of different crystallographic planes of diamond made in another paper by the author have been utilised to give a semi-quantitative form to the theory of crystal shapes of diamond. According to this theory (due to Sir C. V. Raman), diamond is formed by carbon liquified under pressure which retains the shape of the liquid drops with only minor modifications during solidification. Accordingly, the shape of the crystal is controlled by the varying surface tension of the molten liquid in different directions due to the non-random orientation of the valence bonds between the carbon atoms contained in it. It is found possible on this basis to explain various characteristic features of the crystallography of diamond, including especially the preference for certain forms, the influence of the size of the diamond on its shape, and the varying curvature in different zones of the crystal.

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VARIATIONS IN THE ABSORPTION OF INFRA-RED RADIATION BY DIAMOND

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The investigation by Reinkober (1911), of the infra-red absorption spectrum of diamond established that diamonds are not all alike with regard to their infra-red absorption. He noticed the presence of the three bands at 3·0, 4·1 and 4·8 μ in the absorption spectrum of his diamond but failed to record the intense band at 8 μ previously registered by Angstrom (1892) and Julius (1893). More recently Robertson, Fox and Martin (1934), after a detailed investigation of the infra-red absorption of a large number of diamonds, were led to classify the substance into two types I and II, the type I showing the absorption band round about 8 μ which is absent in type II. Recent investigations at this Institute (Raman, *et al.*, 1944) of the various other physical properties of diamond, have however shown that they cannot be described as falling into one or the other of two types only, but show a more diversified behaviour. It appeared probable therefore that the infra-red absorption of diamond should similarly show a diversified behaviour. The present investigation was undertaken to test this idea, and also to obtain quantitative data on the strength of the 8 μ absorption band of diamond for numerous samples. It was also desired to obtain quantitative data on the strength of the absorption band between 4 and 5 μ for some specimens and to see whether any variation, if present, was confined to the 8 μ region alone or also to the region between 4 and 5 μ. The work was greatly facilitated by the use of the flat polished cleavage plates of diamond of which numerous examples were available in Sir C. V. Raman's collection. The present investigation has shown that the strength of the 8 μ infra-red absorption band varies greatly from diamond to diamond, and that such variations are correlated with the behaviour of the specimen in respect of ultra-violet absorption and luminescence. No such variation has, however, been noticed in the region 4–5 μ. Another striking result established by the present research is the existence of patterns of infra-red transparency in individual cleavage plates of diamond closely analogous to the patterns of luminescence and of ultraviolet transparency (Raman, *et al.*, 1944) exhibited by them.

2. Experimental Arrangements

As a source of continuous infra-red radiation, an electrically heated globar element has been used. For detecting the radiation, a thermocouple with a receiver 1·5 millimetre square, which was made in this laboratory, was used in combination with a Hartmann and Braun galvanometer having a coil resistance of 5 ohms and sensitivity of 0·8 millimetre deflection on a scale at one metre distance for one microvolt. In order to monochromatise the radiation for making measurements of absorption coefficients, two different arrangements (*a*) A Residual-ray apparatus and (*b*) An Infra-Red monochromator, have been used.

(*a*) *The Residual Ray Apparatus.*—In this arrangement which is useful only for investigating the 8 μ region, the residual ray band of crystalline quartz which lies in the wavelength range 7·7–9·5 μ is made use of. The radiation from the globar source was reflected two times from surfaces of crystalline quartz at nearly 20° incidence. The radiation thus partially monochromatised by reflections from quartz, was allowed to pass through a one-millimetre aperture before finally being focussed on the thermocouple. The diamond was kept close to the aperture so that the radiation passed through it before falling on the aperture. After passing through the aperture and before falling on the thermocouple the radiation was made to pass through a one-centimetre filter of clear, transparent fluorspar crystal which served to cut off the 20 μ residual rays from quartz and also to further monochromatise the radiation. The radiation finally obtained, occupies a position in the spectrum approximately the same as the 8 μ absorption band of diamond.

(*b*) *The Infra-Red Monochromator.*—This is a rocksalt-prism spectrometer which was recently constructed in this laboratory. The two concave spherical aluminized mirrors used in the instrument are of 9 centimetres clear aperture and 25 centimetres focal length. The 54° prism of rocksalt also made in this laboratory, has got refracting faces about 5 centimetre square. The instrument was used to determine quantitatively the absorption coefficients of a few representative specimens of widely different behaviour in the region 4–5 μ and also to check up by an independent method the results obtained with the Residual-ray apparatus. Using a wide slit (0·5 millimetre for 4–5 region and 1·5 millimetres for the 8 μ region), the monochromator was first adjusted at the peak of either the 4–5 μ band or the 8 μ band of diamond whichever was to be investigated. Then keeping the adjustments fixed, the absorption coefficients were determined for some representative specimens.

For focussing the radiation, wherever not stated, concave (spherical) aluminized mirrors having very high reflectivity for the infra-red were used. The deflections of the galvanometer, which, with both the apparatus, were of the order of a few millimetres could be conveniently measured with a travelling microscope to an accuracy of 0·05 millimetre. The procedure for determining the absorption coefficients consisted in noting the deflections of the galvanometer with and without the diamond in the path of the radiation. For diamonds which do not show appreciable variations of absorption within their areas, the transmission was taken to be the mean of three or more values obtained through different parts within the area of the specimens. Diamonds showing appreciable variations of transparency within their areas were investigated carefully by moving them before the one millimetre aperture of the Residual-ray apparatus between successive readings and noting the transmission and also the portion of the diamond which covered the aperture during each reading. Altogether, thirty-seven cleavage plates of diamond have been examined for their absorption in the 8μ region.

Reinkober (1911) has shown that the reflecting power of diamond for reflection from a single surface, is 16% ($r = 0{\cdot}16$) of the incident energy, for the entire infra-red region between $1{\cdot}0$ to $18{\cdot}0\mu$. The theoretical value of the reflecting power calculated from the expression derived on the basis of the electromagnetic theory is also 17%. Hence it can be safely assumed that if infra-red radiation in the 4–5μ or 8μ region is incident on a plate of diamond, 16% of the energy is lost at every reflection taking place from a diamond-air surface in a direction perpendicular to it. If the diamond be considered to have a thickness t centimetres and an absorption coefficient k per centimetre, then the transmitted fraction of the incident energy σ is given by

$$\sigma = (1 - r)^2 e^{-kt},$$

considering the effect of two reflections only. The quantities σ, r and t being known for a plate of diamond, the coefficient of absorption k per centimetre can be calculated. Since the radiation used for the measurements is not strictly monochromatic, but has a varying intensity distribution in itself, k is the mean coefficient of absorption for this band.

3. Results

The results obtained with different types of diamond are entered in Table I together with the ultraviolet transmission limits of the diamonds for short photographic exposures and the nature of luminescence of the diamond. The results entered in the table can be summarised as follows:—

TABLE I

Absorption and Luminescence of Diamonds

New Catalogue Number	Thickness	Infra-Red Absorption Coefficient in the 8μ Region	Ultraviolet Transmission Limit for short Photographic Exposures	Colour and Intensity of Luminescence
	mm.	per cm.	A.U.	
N. C. 93 ..	0·56	16·5	2950	Weak Blue
N. C. 94 ..	0·59	15·1	3030	Do.
N. C. 98 ..	0·47	14·9	—	Do.
B_3 ..	1·37	12·0	—	Do.
N. C. 99 ..	0·58	10·7	2900	Do.
N. C. 78 ..	1·39	10·2	3100	Moderate Blue
N. C. 177 ..	0·82	10·0	—	Do.
N. C. 77 ..	0·97	9·2	3010	Weak Blue
N. C. 75 ..	0·94	8·6	2950	Do.
N. C. 71 ..	0·79	8·2	2910	Moderate Blue
N. C. 80 ..	0·89	7·6	—	Do.
N. C. 157 ..	0·59	7·6	—	Weak Blue
N. C. 176 ..	1·1?	7·0	—	Moderate Blue
N. C. 74 ..	0·66	6·8	—	Weak Blue
N. C. 92 ..	0·61	6·7	2910	Do.
N. C. 70 ..	2·20	6·5	2950	Intense Blue
N. C. 179 ..	1·18	6·2	—	Moderate Blue
N. C. 79 ..	1·20	5·4	2800	Intense Blue
N. C. 73 ..	0·68	5·4	2830	Weak Blue
N. C. 62 ..	1·50	5·0	2700	Intense Blue
N. C. 126 ..	0·78	4·4	2270	Faint
N. C. 127 ..	0·66	4·0	2660	Do.
N. C. 117 ..	0·87	3·3	2680	Do.
N. C. 122 ..	0·74	1·9	2700	Yellow
N. C. 120 ..	0·78	1·7	2300	Do.
N. C. 124 ..	0·94	1·7	2260	Non-fluorescent
N. C. 121 ..	0·54	1·5	2260	Strong-Yellow
N. C. 89 ..	1·10	1·3	2260	Non-fluorescent
N. C. 125 ..	0·66	0·6	2300	Do.
N. C. 178 ..	0·85	0·6	2250	Do.
N. C. 174 ..	1·62	0·4	2250	Do.
N. C. 60 ..	1·27	0·2	2250	Do.
N. C. 123 ..	0·63	$\lesssim 0$	2260	Do.

— indicates not investigated.

(*a*) The diamonds which absorb most strongly in the region of the 8μ band are those which show a weak blue fluorescence. The infra-red absorption tends to be less for the strongly blue-luminescent diamonds. The absorption coefficient exhibits a wide variation ranging between 5·0 per centimetre and 16·5 per centimetre.

(*b*) Diamonds showing a yellow luminescence or a mixed type of luminescence exhibit infra-red absorption coefficients which are much less than those of blue-luminescent diamonds, the values lying between 2·0 per centimetre and 4·0 per centimetre.

(*c*) Non-luminescent diamonds are highly transparent in the 8 μ region, the loss of energy when this radiation passes through a plate being mostly due to reflection.

(*d*) Allowing for the effect of varying thickness, it is seen that the ultraviolet transmission limit of a diamond progresses further and further into the ultraviolet as the diamond becomes less and less absorbing in the 8 μ region of the infra-red.

In the following Table (II) are reproduced the results of absorption coefficient measurements in the region 4–5 μ together with those obtained for the 8 μ region.

TABLE II

Comparison of Infra-Red Absorptions in the 4–5 μ and 8 μ Regions

New Catalogue Number	4–5μ Region	8 μ Region	
	Monochromator	Monochromator	Residual-Ray Apparatus
	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
N. C. 60 ..	6·8	0·3	0·2
N. C. 174 ..	7·0	—	0·4
N. C. 73 ..	7·7	—	5·4
N. C. 74 ..	7·6	8·7	6·8
N. C. 71 ..	7·1	11·0	8·2
N. C. 77 ..	7·0	—	9·2
B_8 ..	6·8	13·0	12·0
N. C. 94 ..	7·5	—	15·1

— indicates not investigated.

In Table II the values in the second column remain constant within the limits of experimental error. In columns three and four containing the mean absorption coefficients for the 8μ region measured with the Infra-Red monochromator and the Residual-ray apparatus respectively, the values exhibit a wide range of variation. It can be seen that due to the comparative narrowness of the band used with the monochromator, the values given there are higher than those obtained with the Residual-ray apparatus.

4. PATTERNS OF INFRA-RED TRANSPARENCY

Four diamonds out of the thirty-seven cleavage plates examined have been observed to show striking variations in their infra-red transparency within their area. An attempt has been made in Fig. 1 to represent the variations in infra-red transparency for the four diamonds together with their luminescence and ultraviolet transparency patterns. The drawings of

infra-red transparency-variation, made from a visual examination of certain regions of the diamond chosen to cover their full area, are reproduced just to show their similarity to the luminescence and ultraviolet transparency patterns and are not to be regarded as an exact representation of the absorption patterns. However, methods have been devised in this laboratory to obtain photographically the variations in infra-red transparency of diamonds, but as the details have not yet been fully worked out, it is hoped to investigate the question at some later date.

Out of the four diamonds investigated at present, the cleavage plate N.C. 82 (see Fig. 1) shows both blue and yellow luminescence. The central

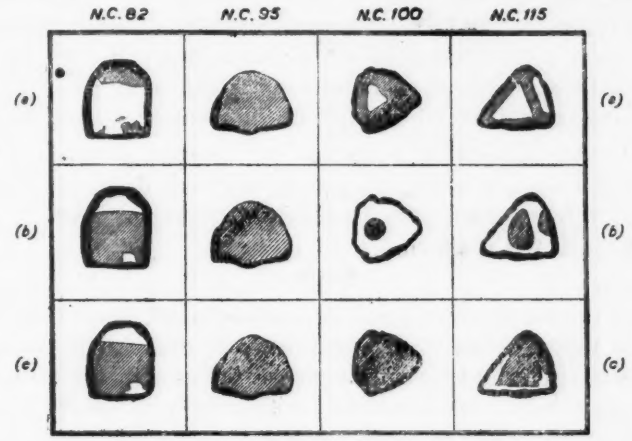

FIG. 1.

(*a*) Patterns of Luminescence. (*b*) Patterns of Infra-Red Transparency.
(*c*) Patterns of Ultraviolet Transparency.

area of the plate shows a fairly bright blue luminescence covered by bands of yellow luminescence. The two extremities of the diamond (top and bottom right-side corner) are non-luminescent and also more transparent to the ultraviolet in the 2536 Å region than the central area. The infra-red absorption coefficient is 5·3 per centimetre in the central part and 1·9 per centimetre at the top non-luminescent area and varies between these values at other regions. N.C. 95 which also shows both blue and the yellow luminescence, has got a gradual variation in the intensity of its luminescence over its area. Observations on infra-red transparency show that the brighter regions in the luminescence photograph correspond to regions more transparent to the infra-red. The diamond N.C. 100 has got a blue luminescent spot in the centre surrounded by non-luminescent area on all sides. The

infra-red transmission through the central spot is lower than in the surrounding area, the coefficients of absorption being 10·0 per centimetre and about 7·0 per centimetre for the two regions respectively. Lastly, the diamond N.C. 115 is again of the mixed type, showing blue and yellow fluorescence. The central triangular area and the narrow strip at one of the sides which are luminescent and opaque to the ultraviolet at 2536 Å are found to be more opaque to the infra-red than the other regions. It is thus quite clear that there is a close correlation with luminescence, and one of a different nature with the ultraviolet transparency. A non-luminescent area must be carefully distinguished from either a weakly blue-fluorescent area or a weakly yellow-fluorescing area. As was shown in Table I, a weakly blue fluorescent diamond is highly opaque in the 8 μ region, while a non-luminescent diamond or one showing weak yellow fluorescence is highly transparent. All these features are shown by diamonds showing infra-red transparency patterns, sometimes one and the same diamond showing all the above-mentioned behaviours.

I take this opportunity to express my heartfelt gratitude to Sir C. V. Raman under whose direction the present work was done. I am also thankful to Dr. R. S. Krishnan whose kind help was always available to me during the progress of this research.

Summary

Using a Residual-ray apparatus, the infra-red absorption coefficients have been measured for 37 cleavage plates of diamond in the 8 μ region. While the absorption coefficients measured with an infra-red monochromator in the region 4–5 μ remain constant within the error of the measurement for all diamonds, those in the 8 μ region show a wide range of variation. The results are correlated with the behaviour of diamond in respect of luminescence and ultraviolet absorption. Some cleavage plates of diamond have also been shown to exhibit patterns of infra-red transparency in the 8 μ region, closely analogous to the patterns of ultraviolet transparency and of luminescence.

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THE ABSORPTION OF ULTRAVIOLET RADIATION BY DIAMOND

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1. Introduction

The early work of Miller (1862) and the later investigation by Peter (1923) showed that while the majority of diamonds completely cut off the ultraviolet radiation below 3000 Å, there were a few which possessed high transparency up to 2250 Å. This finding has been confirmed by Robertson, Fox and Martin (1934) who made extensive investigations on the absorption spectra of both the absorbing and non-absorbing diamonds at different temperatures and discovered several interesting facts. On the basis of their work they also classified diamonds into two categories, the absorbing diamonds showing complete cut-off below 3000 Å and the non-absorbing diamonds which possess high transparency up to 2250 Å. Whereas the previous workers were of opinion that opacity below 3000 Å sets in because of the presence of impurities, these writers attributed it to the strain which they assumed to be present in such crystals. It is however very unlikely that the presence of mechanical strain in any substance can give rise to observable changes in its spectroscopic behaviour. Further, it has been shown very clearly by the investigations carried out recently in this laboratory [Raman and Rendall (1944) and Ramachandran (1944)] that it is precisely those diamonds which absorb strongly in the ultraviolet that are free from any mechanical strain and that form the nearest approach to crystal perfection. The transparent diamonds on the other hand have been found to possess a readily observable mosaic structure. On the basis of these facts it is clear that the observed difference in absorption spectra can be ascribed neither to the presence of chemical impurities, nor to the presence of mechanical strain, but to basic difference in crystal structure.

The recent work of P. G. N. Nayar (1941,' 42) and Miss Sunanda Bai (1944) on the above subject, carried out in this laboratory, have established that the results are of a more diversified character and cannot be described in terms of two alternatives only, as suggested by earlier observers. Working with thin specimens, the thinnest of them being 0·76 millimetre thick,

and by suitably increasing the photographic exposures, Nayar showed that for the so-called ultraviolet opaque diamonds, there was no complete cut-off at 3000 Å and the spectrum could be progressively extended upto 2700 Å. Sunanda Bai found out that for blue-luminescent diamonds the extension of the spectrum transmitted in the ultraviolet depended not only on the thickness of the specimen and the photographic exposures employed but also on the intensity of luminescence. For short photographic exposures, the diamonds showing the mixed type of luminescence transmitted up to 2700 Å, but as the exposure time was increased they showed transmission upto 2250 Å, the strength of absorption increasing rapidly as the limit was approached. The spectrum of the transmitted radiation, far from being continuous, is crossed by a number of absorption lines and bands throughout the recorded range. Some of these were discovered by Robertson, Fox and Martin, many others by P. G. N. Nayar, while some more were added to the list by Sunanda Bai. The behaviour of these lines and bands depended greatly on the strength of luminescence of the diamond. Nayar found that the absorption bands in the region 3000 to 3500 Å were strongest in weakly blue-fluorescent diamonds (*i.e.*, diamonds showing the visible absorption weakly) and *vice versa*. On the other hand, in diamonds showing the mixed fluorescence, Sunanda Bai showed that the bands near 2360 Å behaved in just the opposite manner, appearing strong in strongly luminescent diamonds and weak when the visible luminescence was weak.

The fact that even the most highly absorbing diamonds show a definite photoconductivity with a maximum for exciting wavelength at 2300 Å just as for the highly transparent diamonds, suggests that these should also transmit the ultraviolet upto 2250 Å provided that sufficiently thin specimens are used. The present investigation was undertaken (*a*) to investigate the ultraviolet absorption by the thinnest plates of diamond, (*b*) to trace the variation of the absorption coefficient with wavelength in the range 3100 Å to 2570 Å of a typical blue-luminescent diamond and (*c*) to determine the ultraviolet transmission limits of a number of diamonds in order to correlate this property with the behaviour of the diamonds in the infra-red dealt with in another paper appearing elsewhere in the symposium. It may at once be stated here that the thinnest diamonds of the so-called ultraviolet opaque type have been found, in this investigation, to exhibit transmission upto 2240 Å which is also the limit for the so-called ultraviolet transparent type. Other results which have emerged out of this investigation will be dealt with in the course of the paper.

2. Ultraviolet Absorption Spectrum of the Thinnest Diamonds

One of the two blue-fluorescent specimens which were used for this work, was originally a flat, polished circular cleavage plate of thickness 1·39 millimetres. It was made into a wedge of angle 10° 40′ by the firm of Surajmal. The thinnest portion of this wedge was only 0·12 millimetre thick and so could be used for absorption work to take advantage of its thinness. The diamond, previous to making into a wedge had been shown to have a mean coefficient of absorption of 10·2 per centimetre in the 8·0 μ region of the infra-red. (See paper on variations in the infra-red absorption spectrum of diamond appearing elsewhere in the symposium.) It was also absorbing the ultraviolet below 3000 Å very highly so that spectra obtained with even long exposures extended little below 3000 Å. The other piece which was used for this work is a rectangular plate N.C. 62 which is an intensely blue-fluorescent diamond with its thickness diminishing from 1·5 millimetre at the centre to nearly 0·2 millimetre at the edges by steps. The edges of the plate are in the form of knife-edges with an angle of about 30°. For photographing the absorption spectra through the thinnest portions of a wedge, continuous ultraviolet radiation from a hydrogen discharge tube was first focussed on the diamond attached to the moveable jaw of a slit, the screw cap of which carried a micrometer head. The radiation, deviated by the prismatic wedge, was again focussed on the slit of a medium quartz spectrograph so that a focussed image of the wedge was formed in the plane of the slit. By turning the micrometer head, different portions of the diamond could be brought to focus on the slit. The spectrograph had to be kept tilted by an angle equal to the deviation caused by the wedge. The advantage in having a micrometer head is that absorption spectra can be obtained through different portions of the diamond wedge, beginning from one end and increasing or decreasing the thickness of the absorption path by known amounts.

Results.—Transmission spectra obtained with N.C. 78 through its thinnest portion show clear transmission upto 2240 Å, both at room temperature of the diamond and when it is cooled with liquid air. Beyond 2240 Å there is complete cut-off of the radiation. All efforts to record the spectrum below 2240 Å with long exposures failed to extend the observable transmission beyond that limit. It may be remarked here that the diamond N.C. 78 previous to being made into a wedge (when it was a cleavage plate of thickness 1·37 millimetres) gave transmission spectrum extending very little below 3000 Å.

Transmission spectra obtained with the intensely blue-fluorescent diamond N.C. 62 through the centre of the plate 1·5 millimetres thick extend

upto 2400 Å only, even with very long exposures. The spectra with different times of exposure show, as has been pointed out by Sunanda Bai, a series of step-like falls of intensity at 2900 Å, 2715 Å and 2570 Å, indicating steep rises in the absorption curve. Of all these, the one at 2715 is the most prominent one. The absorption spectrum of the same diamond (N.C. 62) obtained through the thinnest portion of the prismatic edge (about ·25 mm.) shows a transmission upto 2250 Å.

3. Ultraviolet Absorption Bands of Diamond

The absorption spectra of the two diamonds N.C. 78 and N.C. 62 obtained with the specimens kept at room temperature show very intensely the absorption bands at 2364 Å, 2359 Å, 2310 Å and 2298 Å. The former two have been recorded by Sunanda Bai (1944) in the room temperature pictures and all the four in spectra obtained at −180° C. In the present investigation, the room temperature pictures of N.C. 78 in which the conditions were most favourable, have been found to show in addition to the above four bands, two others at 2258 Å and 2246 Å. On cooling the diamond with liquid air, the band at 2298 Å undergoes resolution into two lines, a fainter component appearing on the shorter wavelength side. The two new diffuse

Table I

Ultraviolet Absorption Bands of Diamond

Robertson, Fox and Martin (1934) λ in Å.U.	Sunanda Bai (1944) λ in Å.U.		Present investigation λ in Å.U.	
	29° C.	−180° C.	27° C.	−180° C.
		2405 (*w*)		
		2399 (*s*)		
		2396 (*w*)		
		2395 (*w*)		
		2388 (*w*)		
2363–2359 ..	2364·5	2359·9 (*v.s.*)	2364 (*v.s.*)	2360 (*v.s.*)
	2359·5	2356·5 (*v.s.*)	2359 (*v.s.*)	2355·9 (*v.s.*)
		2314 (*w*)		
2312–2300 ..		2309 – (*s*)	2312 – (*s*)	2309 – (*s*)
		2306	2308	2306
		2300 – (*s*)	2302 – (*s*)	2301 – 2295 (*s*)
		2296	2294	
				2294 (*w*)
				2271·4 (*w*)
			2261 – (*s*)	2260 (*w*)
			2255	
			2248 – (*s*)	2252·8 (*w*)
			2244	2246·5 (*w*)

(*v. s.*) –very strong ; (*s.*)—strong ; (*w.*)—weak.

bands at 2258 Å and 2246 Å have also been found to undergo resolution, a set of four sharp lines appearing in their place. All these features have been recorded for the first time. However, the five absorption bands between 2405 and 2388 Å obtained by Sunanda Bai in diamonds showing the mixed fluorescence could not be recorded in the absorption spectra of N.C. 78. The results are entered above in the Table I.

4. The Absorption Curve of Blue-Luminescent Diamond

Peter (1923) quantitatively determined the absorption coefficient of the highly transparent variety of diamond in the region beginning from the visible and extending into the ultraviolet upto 2250 Å where complete opacity sets in. The curve reproduced by him shows that the absorption coefficient increases continuously from 0·036 per millimetre at 3130 Å to 1·477 per millimetre at 2260 Å without showing any features. Quantitative measurements on the absorption coefficient of the highly absorbing blue-fluorescing diamonds have not been attempted till now.

In the present work, for obtaining the variation of the absorption coefficient with wavelength of a typical blue-fluorescing diamond, the specimen N.C. 78 already referred to was used. A number of spectra were photographed in the same plate by giving equal exposures and running the hydrogen discharge tube at constant current. The diamond was successively moved by means of the micrometer head through equal distances between successive exposures. The distance through which the diamond is moved between two successive exposures is accurately determinable from the known value of the pitch of the micrometer screw. Hence the increment in thickness between successive exposures can also be calculated.

If x and $(x+t)$ centimetres are the thicknesses of the diamond in two successive spectra and if I_1 and I_2 are the intensities of transmitted light in the two cases, the incident light being I in the spectral region λ, the absorption coefficient k per centimetre is given by $I_1/I_2 = e^{kt}$.

The values of I_1 and I_2 required to determine k, were obtained as follows: Absorption spectra were photographed for different thicknesses on a highly contrasting plate (Ilford process plates were used) together with a series of intensity marks given by the method of varying slit-widths. Curves connecting photographic density and logarithm of intensity were drawn for different spectral regions between 2550 Å and 3030 Å. The relative intensities of transmission I_1 and I_2 could be then obtained by microphotometering the spectra and reading off the intensities from the calibration curves. Fig. 1 is a graphical reproduction of the absorption spectrum obtained in

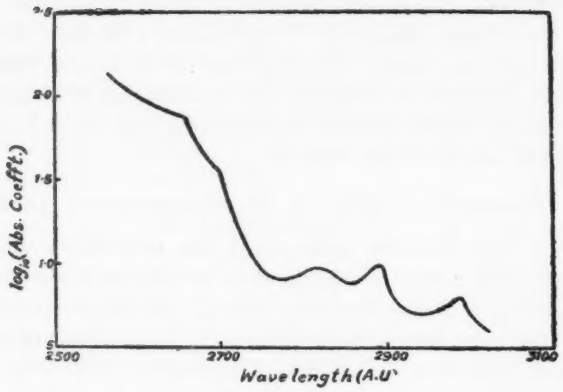

FIG. 1

this manner where the logarithm$_{10}$ (Absorption coefficient) is plotted against wavelength. It can be seen that corresponding to every step-like fall of intensity in the absorption spectrum, there is a steep rise in the absorption curve.

5. Ultraviolet Transmission Limits of Diamonds

The transmission spectra were investigated of the diamonds, whose coefficients of absorption in the infra-red had been determined previously. To establish the degree of correlation existing between ultraviolet and infra-red transparency, the spectra of the diamonds were photographed, giving different exposures for the same diamond on the same plate. The ultraviolet transmission limits of the diamonds for two or three different exposure times together with the infra-red mean absorption coefficients in the $8{\cdot}0\mu$ region and their behaviour in respect of luminescence are reproduced in Table II. It was stated in the introductory part of this paper that the thickness of a cleavage plate is an important factor in deciding the ultraviolet transmission limit of a diamond. This fact was also brought to light in Section 2 of this paper where it was shown that even the most highly absorbing diamond could be made to transmit light upto 2250 Å. While looking at Table II, though it shows in a general manner the correlation between mean infra-red coefficient, the ultraviolet transmission limit and luminescence, the thickness factor should always be borne in mind.

In conclusion, I wish to record my grateful thanks to Sir C. V. Raman under whose inspiring guidance, the present work was done. The diamonds used in this investigation were all from his personal collection.

TABLE II

New Catalogue Number	Thickness	Mean Infra-Red Coefficient	Colour and Intensity of Luminescence	Ultra-violet Transmission Limits		
				Very short Exposures	Short Exposures	Long Exposures
	mm.	$cm.^{-1}$		Å	Å	Å
N. C. 123	0·63	$\lesssim 0$	Non-Luminescent	2260	2250	2240
N. C. 60	1·27	0·2	Do.	2260	2250	2250
N. C. 125	0·66	0·6	Do.	2300	2250	2240
N. C. 89	1·10	1·3	Do.	2260	2250	2245
N. C. 121	0·54	1·5	Yellow	2260	2240	2240
N. C. 120	0·78	1·7	Do.	2360	2255	2250
N. C. 124	0·94	1·7	Non-Luminescent	2260	2250	2250
N. C. 122	0·74	1·9	Yellow	2700	2270	2250
N. C. 117	0·87	3·3	Faint	2680	2310	2250
N. C. 127	0·66	4·0	Do.	2660	2300	2260
N. C. 126	0·78	4·4	Do.	2270	2250	2242
N. C. 62	1·50	5·0	Intense Blue	2700	2450	2380
N. C. 62	0·25*	5·0	Do.	—	—	2250
N. C. 73	0·68	5·4	Weak Blue	2830	2650	2400
N. C. 79	1·20	5·4	Intense Blue	2800	2650	—
N. C. 70	2·20	6·5	Do.	2950	—	2400
N. C. 92	0·61	6·7	Weak Blue	2910	2740	2580
N. C. 157	0·59	7·6	Do.	2870	2730	2650
N. C. 71	0·79	8·2	Medium Blue	2910	2780	—
N. C. 75	0·94	8·6	Weak Blue	2950	2850	—
N. C. 77	0·97	9·2	Do.	3010	2880	—
N. C. 78	1·39	10·2	Medium Blue	3100	2940	—
N. C. 78	0·12*	10·2	Do.	—	2240	2240
N. C. 99	0·58	10·7	Weak Blue	2900	2780	—
N. C. 94	0·59	15·1	Do.	3030	2830	—
N. C. 93	0·56	16·5	Do.	2950	2810	—

*—Approximate thickness. — —Transmission limit not determined.

SUMMARY

The thinnest diamonds of the so-called ultraviolet opaque type have been shown to exhibit transmission upto 2240 Å which is also the limit for the so-called ultraviolet transparent type. In a diamond showing blue luminescence, five new absorption bands have been discovered for the first time in the region below 2300 Å. The variation of absorption coefficient with wavelength for a typical blue-luminescent diamond has been determined for the first time in the region 3030 Å–2570 Å. Finally, the ultraviolet transmission limits for a number of diamonds have been obtained for different photographic exposures and the data correlated with their luminescence and mean infra-red absorption coefficient in the 8 μ region.

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Description of Plates

Plate XI

Fig. 1. Ultraviolet Transmission Limits of Blue-Fluorescent Diamond (N.C. 78) for different thicknesses (*a*) 0·15 mm. (*b*) 0·30 mm. and (*c*) 0·37 mm.

Fig. 2. Ultraviolet Transmission Limits of Strongly Blue-Fluorescent Diamond (N.C. 62) for (*a*) Very short photographic exposure; (*b*) Short photographic exposure; (*c*) Long photographic exposure and (*d*) Small absorption path 0·25 mm.

Plate XII

Fig. 3. Micro-photometric curve of the Ultraviolet Absorption Spectrum of Blue-Fluorescent Diamond (N.C. 78) at Liquid Air Temperature.

Fig. 4. Ultraviolet Absorption Spectrum of Thin Blue-Fluorescent Diamond (N.C. 78): (*a*) At Room Temperature; (*b*) At Liquid Air Temperature.

Fig. 5. Ultraviolet Absorption Spectrum of (*a*) Green-Fluorescent Diamond N.C. 151 and (*b*) Non-Fluorescent Diamond N.C. 126.

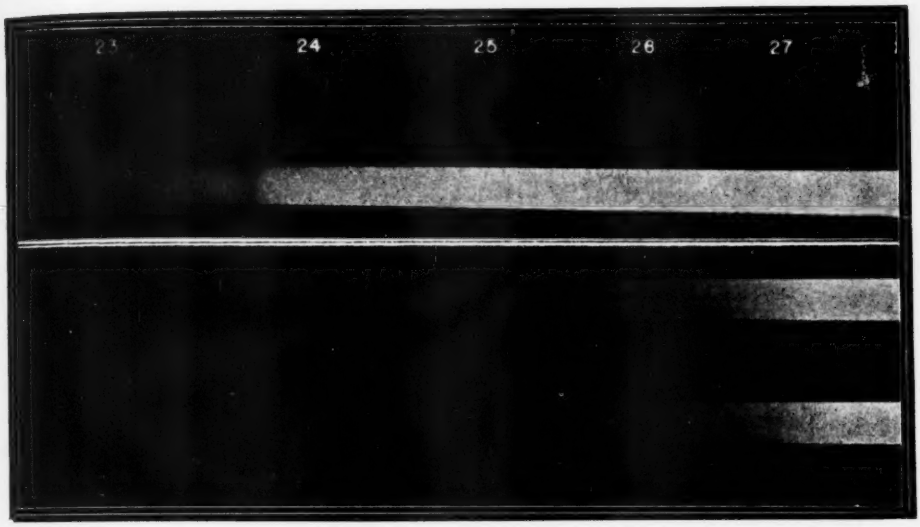

FIG. 1

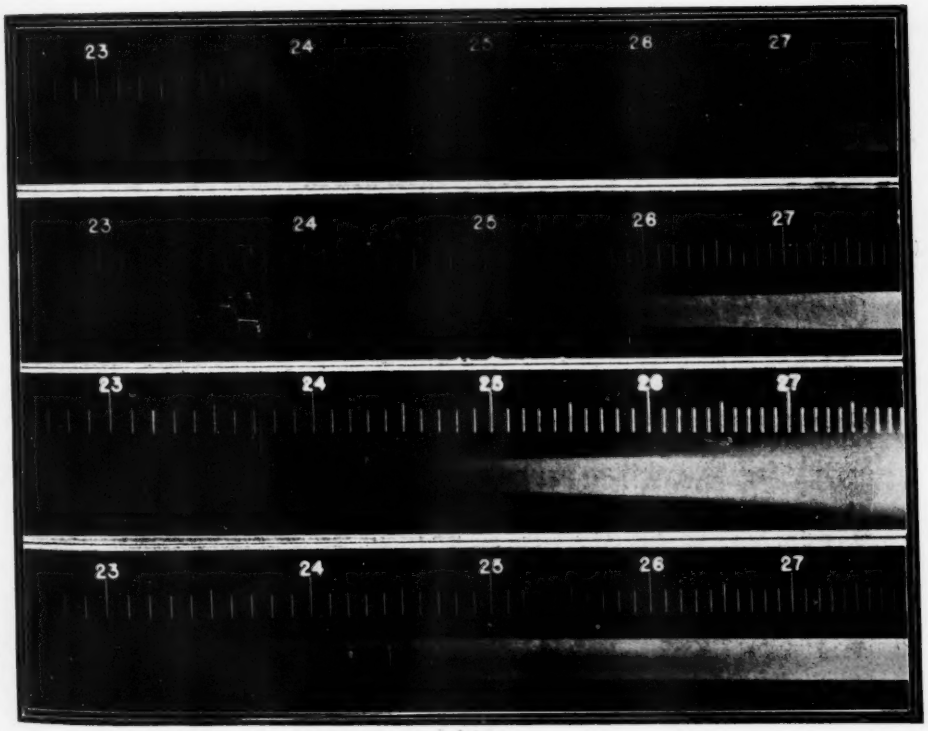

FIG. 2

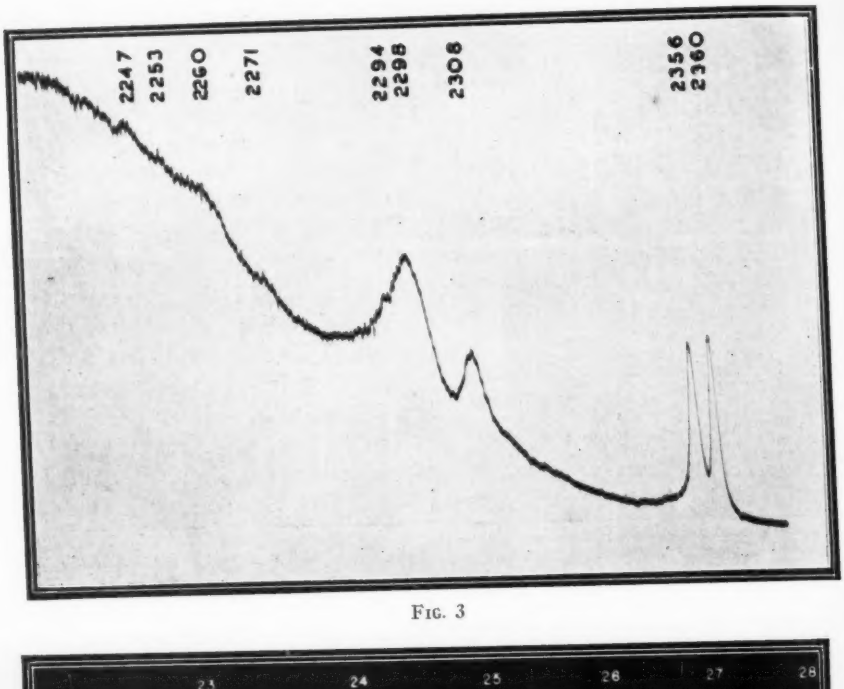

FIG. 3

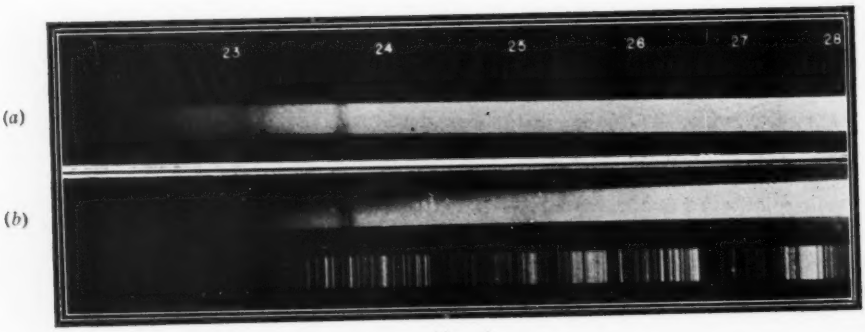

FIG. 4

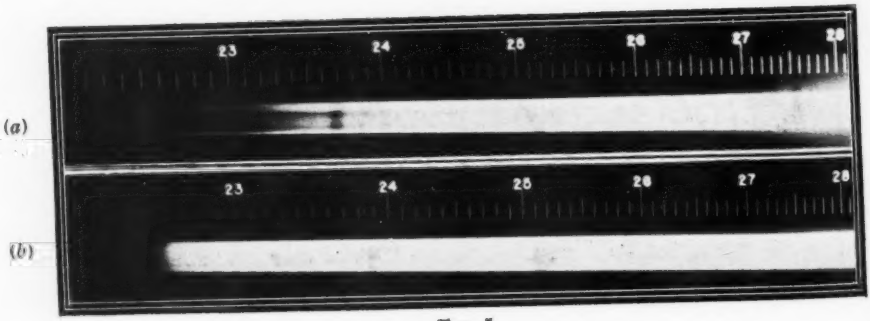

FIG. 5

THE ABSORPTION SPECTRUM OF DIAMOND IN THE VISIBLE REGION

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1. Introduction

Walter (1891) who first noticed the line at 4155 Å in the absorption spectrum of diamond, attributed it to the presence of impurities. A fluorescent emission at the same wavelength and hence presumably having the same origin was noticed by the early workers on the Raman spectrum of diamond. Robertson, Fox and Martin (1934) who investigated the absorption spectra of numerous diamonds, detected the presence of the 4155 Å line in only one of their specimens and so were led to dismiss the fact as a rare occurrence not characteristic of diamond, but probably due to the presence of impurities. That the situation is, in reality, quite different became evident from the investigations at liquid air temperatures made at this Institute. P. G. N. Nayar (1942) found that the 4152 Å line appeared both in emission and in absorption with all the diamonds examined by him, though with enormously different intensities in the different specimens, and that it is accompanied by a subsidiary set of lines and bands appearing at longer wavelengths in fluorescence and at diminished wavelengths in absorption. The latter were interpreted as arising out of the combinations of the lattice frequencies of diamond with the most intense electronic line at 4152 Å. Miss Mani (1944) investigated the behaviour of numerous diamonds including some non-luminescent ones and established by her studies that while non-luminescent diamonds show no absorption, the 4152 Å system is characteristic of blue fluorescence as shown by Nayar and that yellow fluorescence is characterised by an electronic emission at 5032 Å together with a subsidiary system due to lattice vibrations analogous to the 4152 Å system. In addition to the 4152 Å and 5032 Å lines and the systems associated with them, Miss Mani showed that several electronic lines were present, some of them appearing in absorption while most of them appeared in fluorescence. Some of these lines were characteristic of blue fluorescence, others of yellow fluorescence, while there were some others appearing in both blue and yellow fluorescent diamonds.

The intensity with which an electronic line appears in absorption depends both on the intrinsic strength of the absorption and the length of

path available. While it is possible to record even very weak electronic lines in emission by prolonging the exposure, such lines can be recorded in absorption only when the conditions are favourable. The results of Miss Mani suggested that by the use of large thicknesses of diamond for absorption work, one would probably be able to obtain all the electronic lines in absorption also. The present work was undertaken to investigate the absorption spectra of large thicknesses of diamond and to see whether the many electronic lines observed in the spectrum of fluorescence could be observed in absorption also. The work was greatly facilitated by the availability of four large, circular cleavage plates of diamond B_1, B_2, B_3 and B_4 each one of them being about a centimetre and a half in diameter and of thickness ranging between 1·2 and 1·6 millimetres. It may be mentioned here that as a result of the present investigation, several electronic lines appearing in the spectrum of blue fluorescence have been observed in absorption also; several new absorption lines have also been discovered which were not recorded previously either in fluorescence or in absorption. Another interesting fact observed here is that by employing large thicknesses of diamond, the light is completely cut-off below the 4152 Å line.

2. Method of Investigation

Nayar and Miss Mani used diamonds edgewise to obtain large absorption paths. In the present investigation the use of the "Multiple Transmission Method" has enabled still larger paths to be obtained. The four plates of diamond were kept close together such that they formed an assembly of total thickness nearly 6 millimetres. The whole assembly was then sandwiched between two brass plates in which two small holes were cut so that light could be allowed to enter the system through one of the holes and after multiple transmission inside the diamonds, the emergent light could be made to come out through the second hole in the other brass plate. Aluminium foil was attached to the brass plates to reflect the radiation after each transmission through all the four plates in the system. In this manner an absorption thickness of several centimetres (3·0 centimetres for four internal reflections) could be easily secured. It would have required a Cullinan diamond to have secured such large absorption paths in the ordinary way. For working at low temperatures, the whole assembly was put inside a copper block and the block screwed on to the bottom of the brass inner vessel of a demountable Dewar flask. The interspace was continually evacuated by a Cenco Hyvac pump and liquid air was poured in the inner vessel to cool the diamonds to $-180°$ C.

As a source of continuous radiation, an incandescent lamp with a straight filament was used. A medium quartz spectrograph was first used

to photograph the spectra, but later when higher dispersion seemed desirable, a Fuess glass spectrograph was used. The results obtained are described below.

3. Experimental Results

(*a*) *Limit of Transmission.*—At room temperature, the absorption spectra showed a complete cut-off of all radiations with wavelengths below 4160 Å. The cut-off was not sharp, but the transmitted intensity decreased gradually as 4160 Å was approached. Even with long photographic exposures the spectrum could not be extended below 4160 Å. When the diamonds were cooled with liquid air, the cut-off at 4160 Å became very sharp as can be seen from the photograph reproduced [Fig. 1 (*b*) in Plate XIII].

(*b*) *Sharp Electronic Lines.*—The second column of Table I gives a list of the electronic absorption lines and bands recorded in spectra obtained at − 180° C. The third, fourth, fifth and sixth columns show the results of Miss Mani and are given here for comparison. Most of the lines observed by Miss Mani in the fluorescence spectrum of blue-luminescent diamonds have been recorded in the present work. In addition, several other electronic lines which could not have been observed in the fluorescence because of their overlapping with the lattice spectrum accompanying the 4152 Å line have also been recorded in the absorption spectra obtained with a large thickness of diamond. On the other hand, the 5032 Å absorption line and the whole system associated with it, have not appeared in these spectra even under these favourable conditions. The intense electronic line at 4277 Å, which has been identified by Miss Mani as characteristic of yellow fluorescence has also not been recorded here. It must be mentioned here that all the diamonds used in this work except one are purely blue-luminescent specimens. One of the four diamonds shows some yellow fluorescent patches in addition to its blue fluorescence.

(*c*) *Broad Absorption Bands.*—Miss Mani observed in a single diamond N.C. 70 three broad absorption bands at 4516 Å, 4652 Å and 4776 Å. In the absorption spectra obtained in this investigation with large thicknesses of diamond, these three bands appear very intense. This suggests that the three broad bands are characteristic of all blue-fluorescing diamonds and not the peculiarity of an exceptional specimen.* The measurements of the bands are contained in Table II.

---

* Miss Mani has reproduced in her paper, the absorption and fluorescence spectra of this specimen D. 32 (N.C. 70). While the 4152 Å line appears with great strength in absorption, it is scarcely noticeable in the emission spectrum reproduced, its intensity being evidently reduced almost to vanishing point by self-reversal. This supports the inference made from the present investigation that the three bands are characteristic of blue fluorescence, but are observable only when the absorption is of adequate strength.

TABLE I

Sharp Electronic Absorption Lines observed at − 180° C. in Thick Diamonds

Description of line	Wavelength	Blue-Fluorescing Diamonds		Yellow-Fluorescing Diamonds	
		Luminescence	Absorption	Luminescence	Absorption
	A. U.	A. U.	A. U.	A. U.	A. U.
Band { edge	4141				
Band { peak	4151	4152	4152	4152	4152
Band { edge	4162				
Weak	4168	—	—	—	—
..	—	—	—	4175	—
Medium	4185	4189	4189	—	—
Do.	4198	4197	4197	—	—
Strong	4205	4206	4206	—	—
Weak	4216	—	—	—	—
Medium	4223	—	—	4222	—
—	—	†4227	—	4227	—
Medium	4233	—	—	4232	—
Strong	4250	—	—	—	—
—	—	—	—	4277	—
Strong	4307	—	4304	—	—
Weak	4317	—	—	—	—
Medium	4335	—	—	—	—
Do.	4354	—	—	—	—
Strong	4378	—	4380	—	—
—	—	*4388	—	4388	—
Medium (Diffuse)	4397	—	—	—	—
Medium	4621	—	—	—	—
—				4907	4907
No absorption observed in the region between 4800 A.U. and 6500 A.U.		†4959	†4959	4959	4959
		†5032	†5032	5032	5032
		—	—	5359	5359
		—	—	5658	—
		—	—	5695	—
		—	—	5758	—
		—	—	6177	—
		—	—	6265	—
		—	—	6358	—

*—Observed in one diamond only.

†—Observed in some diamonds but not in other typically blue-fluorescent specimens.

TABLE II

Absorption Bands in Blue-Fluorescing Diamonds

Description	Wavelength	Measurement of Bands by Miss Mani
	A. U.	A.U.
Medium { edge ..	4466	4494
Medium { peak ..	4512	4516
Medium { edge ..	4558	4538
Weak { edge ..	4586	4602
Weak { peak ..	4625	—
Weak { edge ..	4682	4701
Intense { edge ..	4754	4758
Intense { peak ..	4776	—
Intense { edge ..	4797	4794

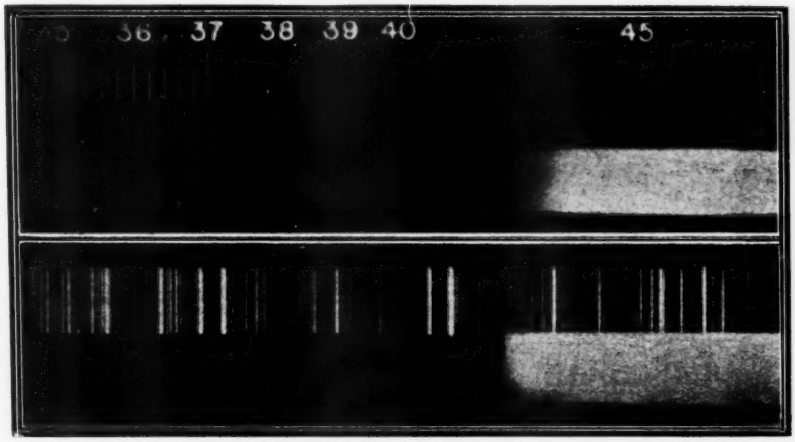

FIG. 1. Absorption of Visible Light by Thick Diamond

(a) At Room Temperature

(b) At Liquid Air Temperature

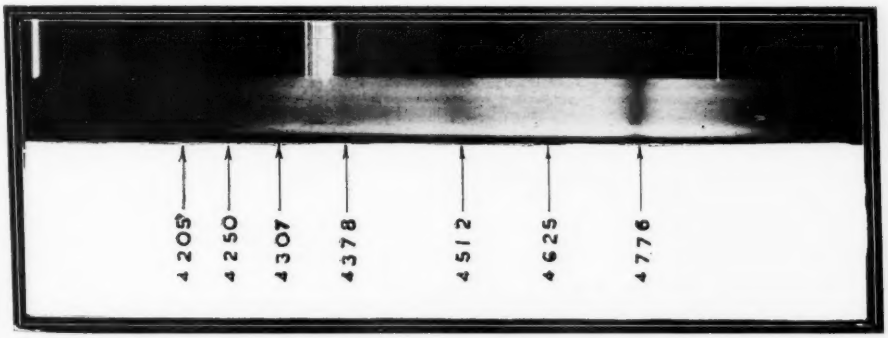

FIG. 2 Absorption of Visible Light by Thick Diamond under High Dispersion

In conclusion, I wish to record my grateful thanks to Sir C. V. Raman for the able guidance and kind encouragement he gave me during the progress of the work.

Summary

The absorption spectrum of diamonds exhibiting a weak blue fluorescence has been investigated in the visible region with large absorption paths secured by the method of multiple transmission. With thicknesses of the order of a few centimetres, the radiation is completely cut-off below 4160 Å. At the temperature of liquid air, a whole series of electronic absorption lines have been observed in the visible spectrum, several of them for the first time. Three absorption bands centred at 4512 Å, 4625 Å and 4776 Å have also been recorded which had been previously noticed only in one specimen having an exceptionally strong absorption.

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THE INFRA-RED ABSORPTION SPECTRUM OF DIAMOND

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1. Introduction

In a paper (Ramanathan, 1946) appearing earlier in this symposium, it is shown that the infra-red absorption of diamond exhibits a diversified behaviour in the 8 μ region of the spectrum. On the basis of quantitative measurements contained therein, diamonds have been broadly classified as falling into one or the other of four groups related to the behaviour of diamond in respect of luminescence, *viz.*, (*a*) Weakly blue-fluorescent diamonds exhibiting a high coefficient of absorption in the 8 μ region; (*b*) Strongly blue-fluorescent diamonds in which the absorption comes down; (*c*) Diamonds showing blue and yellow fluorescence in which the absorption is still less; and (*d*) Non-fluorescent diamonds, which, after correcting for reflection, are non-absorbing in the 8 μ region. The need for investigating the absorption spectrum in the near infra-red of typical specimens representing each one of the above four groups, was felt because of the lack of previous work on the subject relating it to the property of luminescence. Also, with our present knowledge of the several other physical properties of diamond, it is easy to see that the investigations on the infra-red absorption spectrum of diamond carried out till now have been made with unsatisfactory specimens. The so-called Type II diamonds (D. 2 and D. 22) of Robertson, Fox and Martin (1934) show photoconductivity maxima at 3300 Å which is characteristic of their Type I diamonds. In the ultraviolet region, D. 2 begins to absorb appreciably even at 2350 Å. It is not surprising therefore, that in the 8 μ region of the infra-red, the so-called transparent diamond D. 2, for which a curve has been reproduced by the above authors, shows only about sixty per cent. transmission. Sutherland (1945) remarks that his three so-called transparent diamonds were 'admittedly of a "rough" nature', all of them showing a complete black-out in the region 4·5 to 5·0 μ and less than one or two per cent. transmission in other regions.

For the present work, a large number of cleavage plates of diamond, excellently suited for work of this kind, was available for choice in Sir C. V.

Raman's collection. Even with very short photographic exposures, the spectrum transmitted in the ultraviolet by the typical non-luminescent diamonds extend upto 2250 Å. In what follows, the investigation of the infra-red absorption spectra of four typical diamonds, each one representing one of the abovementioned four groups is described in detail. It may be mentioned here, that as a result of the present investigation the principal lattice vibration of diamond with a frequency of 1332 cm.$^{-1}$ has been recorded in absorption for the first time in the luminescent diamonds investigated and has been found to be absent in the non-luminescent diamond. Also, the non-luminescent diamond after allowing for reflection, is found to be hundred per cent. transparent in the region between 770–1400 cm.$^{-1}$ Other interesting observations made in this investigation will be described in the course of the paper.

2. Experimental Technique

The source of continuous infra-red radiation and the rock-salt prism spectrometer have already been described in the paper referred to in the introduction. In the present investigation a Boy's radiomicrometer constructed in this laboratory has been used for detecting the radiation. The instrument was fitted with a rock-salt window for making it air-tight. The use of a fairly thick quartz fibre for the suspension resulted in steady working of the instrument. The deflections in the 8 μ region with a slit-width of a quarter of a millimetre were of the order of 6 centimetres and could be read to an accuracy of 0·05 centimetre. For calibrating the instrument, the well-known absorption peaks of diamond at 1285 and 1208 cm.$^{-1}$ have been used as standards. During the present work, more care was devoted in obtaining a correct contour of the 8 μ absorption band in the different diamonds than in determining the exact positions of the absorption peaks.

The procedure for obtaining the absorption curve of a diamond consisted in traversing the spectrum before the exit slit of the instrument by setting the spectrometer at frequent intervals of wavelength. At each setting of the spectrometer, the percentage of radiation cut-off by the diamond was obtained by taking the mean of eight readings which gave a value for the percentage cut-off correct within half a per cent. in the 8 μ region of the spectrum. A very simple lever mechanism served to bring the diamond in the path of the radiation always to the same position before the entrance slit of the spectrometer. With regard to the wavelength measurements, the accuracy can be judged from the positions at which the other well-known absorption peaks at 1376, 1105 and 1013 cm.$^{-1}$ appear in three of the curves reproduced. The results obtained in the investigation are described below.

3. Experimental Results

Nature of the 8 μ Band.—

(*a*) *Weakly Blue-Fluorescent Diamond.*—The absorption curve (Fig. 1) for the diamond N.C. 71 (thickness 0·78 mm.) shows that the 8 μ band is a little more intense than the band appearing at 5 μ (2000 cm.$^{-1}$). The general nature of the curve is very similar to the absorption curves obtained by previous investigators for the so-called Type I diamonds, except for the fact that there is evidence of two new absorption peaks at 1330 cm.$^{-1}$ and 1150 cm.$^{-1}$ in the curve reproduced for N.C. 71.

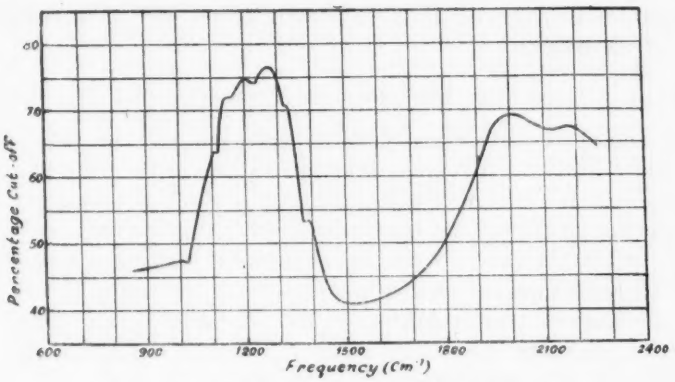

Fig. 1. Infra-Red Absorption Spectrum of N.C. 71

(*b*) *Non-Luminescent Diamond.*—The absorption curve (Fig. 2) of N.C. 60 (thickness 1·27 mm.) shows a uniform transmission of 74% in the region between 7 μ and 13 μ. Accepting Reinkober's (1911) value of the reflection coefficient ($r = 0{\cdot}16$) we should expect a transmission of only 72% even for completely transparent diamonds. As the difference of 2% is not within the error of the measurements, the discrepancy is likely to be due to the slight focussing action of light which the diamond possessed probably due to the curvature of its faces.

(*c*) *Intensely Blue-Luminescent Diamond.*—In Fig. 3 is shown the absorption curve of N.C. 79 (thickness 1·20 mm.) . The peak value of the absorption in the 8 μ region is slightly lower than the value in the 5 μ (2000 cm.$^{-1}$) region. While some of the individual peaks come out very prominently in the absorption spectrum of this diamond, the two well-known maxima at 1208 and 1285 cm.$^{-1}$ are weaker in intensity than 1332 cm.$^{-1}$

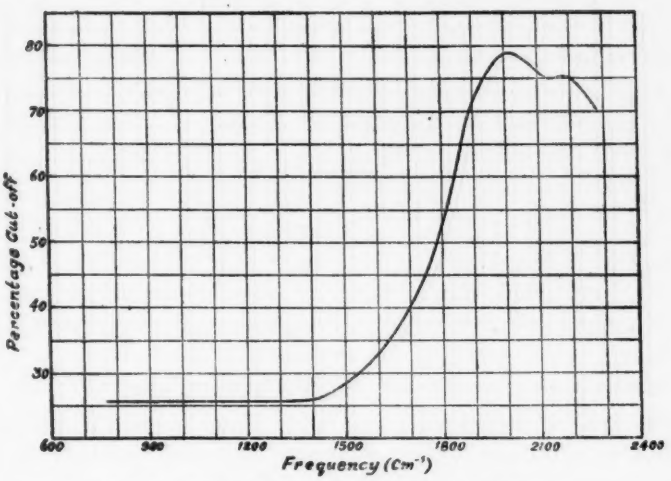

FIG. 2. Infra-Red Absorption Spectrum of N.C. 60

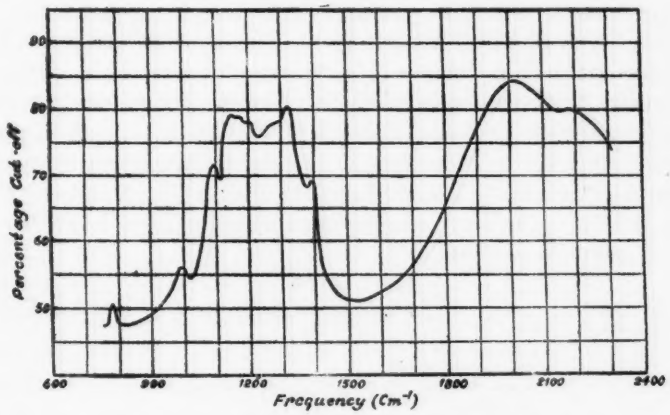

FIG. 3. Infra-Red Absorption Spectrum of N.C. 79

(*d*) *Diamond Luminescing Blue and Yellow with Great Intensity.*—In this diamond with a thickness of 0·80 mm. (Fig. 4), the peak absorption in the 8 μ region is much less than the value in the 5 μ region. Here again there appears a change in the distribution of intensity in the band.

Absorption Maxima.—The principal lattice vibration with a frequency of 1332 cm.$^{-1}$ has been recorded for the first time in the luminescent diamonds investigated. As was mentioned in the introductory part of the paper, the

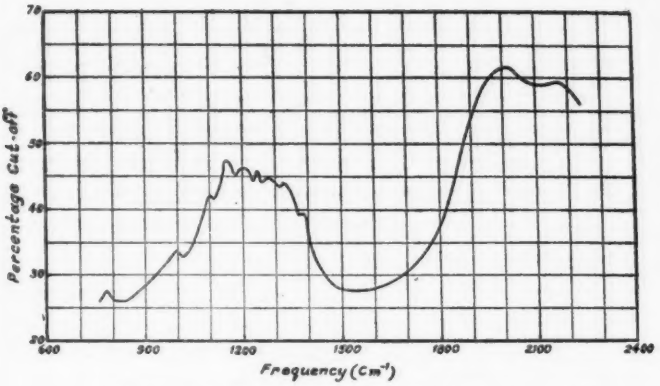

FIG. 4. Infra-Red Absorption Spectrum of N.C. 110

failure to record the band previously might be due to the use of unsatisfactory specimens of diamond. The difficulty in recording the band in a weakly blue-fluorescent diamond is that the band appears as a small kink in the curve which is likely to be mistaken for a fluctuation in the intensity of the source or some error in observation. By the use of a globar which, in virtue of its large heat capacity, has got a very constant infra-red radiancy and by taking the mean of a number of observations for each setting of the spectrometer, the above sources of error have been eliminated in the present work. In addition to the 1332 cm.$^{-1}$ absorption peak, a few other peaks have been observed to be present in the absorption spectra of the intensely luminescent diamonds. The values of the frequencies of these peaks, which are not claimed to be very accurate, are entered in Table I together with the results of previous workers.

TABLE I

Frequencies observed in Infra-Red Absorption in the 8 μ *Region*

Robertson, Fox and Martin (1934)	Sutherland and Willis (1945)	Present Work
cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
—	784	780
—	1013	1000
—	1105	1100
—	—	1150
—	—	1170
1208	1208	1208
—	—	1245
1289	1285	1280
—	—	1325
1372	1376	1385

The 5 μ Band.—

The absorption curves for the four diamonds are identical in contour in the 5 μ region. Also, apart from minor deviations, they are positioned according to the requirements of the thicknesses of the diamonds. In all the three luminescent diamonds it can be seen that the minimum of absorption between the 5 μ and the 8 μ bands is roughly at about 1550 cm.$^{-1}$ This is due to the overlapping of the 5 μ and the 8 μ bands and it can also be seen from Fig. 2 where the 8 μ band is completely absent, that the 5 μ band starts really at about 1400 cm.$^{-1}$ This position is a little less than double the fundamental lattice frequency at 780 cm.$^{-1}$ observed in two of the diamonds. The two peaks appearing at 2010 cm.$^{-1}$ and 2180 cm.$^{-1}$ are undoubtedly the octaves of the next two vibrations appearing in Table I with frequencies 1000 cm.$^{-1}$ and 1100 cm.$^{-1}$ Hence we are justified in concluding that the absorption peaks appearing in the 8 μ band are the fundamental frequencies and those appearing in the 5 μ band the octaves and combinations of the same frequencies. Due to the inadequacy of the resolving power of the instrument used, the measurements could not be pushed beyond 2200 cm.$^{-1}$ with any advantage. Also, for the same reason, the finer details observed by Robertson, Fox and Martin (1936) in the 5 μ region, could not be recorded here.

4. Interpretation of Results. The 8 μ Band

(*a*) *Principal Lattice Vibration.*—The fundamental vibration of the diamond structure with a frequency of 1332 cm.$^{-1}$ represents the oscillation of the two interpenetrating lattices of carbon atoms against each other. If we regard the unit cell containing two non-equivalent atoms to possess either tetrahedral or octahedral symmetry, then the activity of the lattice vibration in Raman effect and infra-red absorption can be obtained by an application of the principles of group theory. If the symmetry is tetrahedral, then as can be seen from Table II, the triply degenerate mode F_2 which represents the lattice vibration, will be active both in Raman effect and infra-red absorption.

If, on the other hand, the symmetry is octahedral (Table III), then the triply degenerate mode F_{2g} which represents the same lattice vibration will be active in Raman effect but inactive in infra-red absorption. In fact for the octahedral symmetry, the selection rules for Raman effect and infra-red absorption are complementary, the modes appearing in scattering being inactive in absorption and *vice versa*. The non-luminescent diamond investigated here for which the absorption curve is reproduced in Fig. 2 is found to be completely non-absorbing in the region between 770 cm.$^{-1}$

TABLE II

** Symmetry operations pertaining to the Td group are E, $8C_3$, $3C_2$, 6σ and $6S_4$*

T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$	n_i	n_i'	Selection Rules	
								Raman	Infra-Red
A_1 ..	1	1	1	1	1	0	0	—	—
A_2 ..	1	1	1	−1	−1	0	0	—	—
E ..	2	−1	2	0	0	0	0	—	—
F_1 ..	3	0	−1	−1	1	0	0	—	—
F_2 ..	3	0	−1	1	−1	2	1	Active	Active
U_R ..	2	2	2	2	2				
$h_j x_j$ ..	6	0	−6	12	−12				
$h_j \psi_j'$ ..	0	0	0	12	−12				

* The symbols used in this and in the following table are the same as those given in *Scattering of Light and Raman Effect*, by Prof. S. Bhagavantam (Andhra University Publication, 1940).

TABLE III

The symmetry operations pertaining to the O_h group are E, $8C_3$, $3C_2$, 6σ, $6S_4$, i, $8S_6$, 3σ, $6C_2$ and $6C_4$

O_h	E	$8C_3$	$3C_2$	6σ	$6S_4$	i	$8S_6$	3σ	$6C_2$	$6C_4$	n_i	n_i'	Selection Rules	
													Raman	Infra-Red
A_{1g} ..	1	1	1	1	1	1	1	1	1	1	0	0	—	—
A_{2g} ..	1	1	1	−1	−1	1	1	1	−1	−1	0	0	—	—
E_g ..	2	−1	2	0	0	2	−1	2	0	0	0	0	—	—
F_{1g} ..	3	0	−1	−1	1	3	0	−1	−1	1	0	0	—	—
F_{2g} ..	3	0	−1	1	−1	3	0	−1	1	−1	1	1	Active	Inactive
A_{1u} ..	1	1	1	1	1	−1	−1	−1	−1	−1	0	0	—	—
A_{2u} ..	1	1	1	−1	−1	−1	−1	−1	1	1	0	0	—	—
F_{1u} ..	2	−1	2	0	0	−2	1	−2	0	0	0	0	—	—
F_{1u} ..	3	0	−1	−1	1	−3	0	1	1	−1	0	0	—	—
F_{2u} ..	3	0	−1	1	−1	−3	0	1	−1	1	1	0	—	—
U_R ..	2	2	2	2	2	0	0	0	0	0				
$h_j x_j$ ..	6	0	−6	12	−12	0	0	0	0	0				

and 1400 cm.$^{-1}$ At the same time, it shows a sharp line at 1332 cm.$^{-1}$ in Raman effect. We are therefore justified in assigning the octahedral symmetry to the non-luminescent diamonds which show a triply degenerate Raman-active frequency in light scattering but no corresponding infra-red absorption maximum. All the luminescent diamonds investigated (Figs. 1, 3 and 4) show an absorption peak at 1332 cm.$^{-1}$, this being strongest in the weakly blue-fluorescent diamond. Since the triply degenerate mode appears both in Raman effect and infra-red absorption in the luminescent diamonds,

the appearance of the 1332 cm.$^{-1}$ peak should be ascribed to the tetrahedral symmetry of the crystals.

That diamond may be either tetrahedral or octahedral in symmetry is not an *ad hoc* hypothesis. One has only to study the crystallographic evidence set out in the introductory paper of the present symposium to appreciate the position in this respect correctly. Further, it is an indisputable fact that the diamonds which show the infra-red absorption in the 8 μ region are precisely those which are most nearly free from chemical impurities and which form the nearest approach to crystal perfection, while the diamonds which do not show this absorption band exhibit characteristic irregularities of structure. Hence, the appearance of the absorption band and its absence respectively in the two cases cannot be ascribed to crystal imperfections or other adventitious circumstances, and must be due to fundamental difference in *crystal symmetry*.

When interpenetration of the positive and negative tetrahedral forms occurs, the crystal structure must, in strictness, be considered as deviating from tetrahedral towards octahedral symmetry to an increasing extent as the interpenetration is on an increasingly finer scale. Such interpenetration would also result in an appreciable inhomogeneity of structure which would be favourable for the development of luminescence. As is shown in other papers appearing in the symposium, this explanation of the origin of blue luminescence is confirmed by various other lines of experimental evidence. Hence, also, we should expect that with increasing intensity of blue luminescence, the infra-red absorption should show a distinct weakening. The fact that for the strongly blue-fluorescent diamond N.C. 79, the absorption in the 8 μ region shows a lower value than what we should expect if it were weakly blue-fluorescent, thus affords support for the interpenetration theory of blue luminescence (Raman, 1944). If a diamond is a mixture of tetrahedral and octahedral varieties, then it should show even a still lower value of absorption in the 8 μ region, and that is what is actually observed for the specimen N.C. 110 (Fig. 4). Hence the infra-red data for the yellow luminescent diamonds provide independent evidence that the tetrahedral and octahedral varieties appear intertwinned in such diamonds.

(*b*) *Superlattice Vibrations.*—An application of the group theory to a superlattice having twice the dimensions (eight times the volume) of the unit cell (Bhagavantam, 1943) results in eight modes of vibration of which one is the same as the lattice vibration 1332 cm.$^{-1}$ The seven other superlattice frequencies are disallowed in Raman effect and infra-red absorption irrespective of whether the symmetry of the crystal is tetrahedral or octahedral.

Working at liquid air temperatures, Nayar (1942) and Miss Mani (1944) have observed these superlattice frequencies in the absorption and emission spectra of diamonds in the visible region, these appearing in combination with the two principal electronic lines at 4152 and 5032 Å. In the infra-red absorption spectrum of the non-luminescent (octahedral) diamond investigated, the principal lattice frequency 1332 cm.$^{-1}$ as well as the superlattice frequencies are absent as fundamentals. This is in perfect accord with the selection rules. On the other hand, several discrete absorption maxima are found to be present in the absorption curves of the luminescent diamonds in addition to the 1332 cm.$^{-1}$ peak. The positions of most of these peaks agree reasonably well with the superlattice frequencies obtained by Nayar and Miss Mani. Still, we cannot completely identify them with the vibration frequencies of the superlattice unless and until the infra-red absorption measurements are carried out at the temperature of liquid air. In the following table (Table IV) are reproduced the positions of the infra-red absorption maxima together with the frequencies observed by Miss Mani in absorption and luminescence in the visible region. The figures within brackets refer to those which are very weak.

TABLE IV

Superlattice Frequencies of Diamond

Infra-Red Absorption	Luminescence and Visible Absorption
cm.$^{-1}$	cm.$^{-1}$
—	565
780	784
—	(848)
—	(946)
1000	1013
1100	1088
—	1131
1150	1149
1170	—
1208	1218
1245	1252
1280	1284
1325	1330
—	1341
—	1361
1385	1387

It will be seen from the table that the observed infra-red absorption maxima agree fairly well with those observed in luminescence and visible absorption. The position regarding the superlattice frequencies can be stated as follows: (1) They appear in infra-red absorption when the fundamental lattice vibration (1332 cm.$^{-1}$) is active. (2) They are absent when the

1332 cm.$^{-1}$ vibration is inactive. (3) Their intensities are roughly of the same order of magnitude as that of the 1332 cm.$^{-1}$ vibration. (4) Those superlattice frequencies appear most strongly which are nearest to the principal lattice frequency, while those which are remote from it appear only weakly. (5) The entire absorption is of an order of magnitude very small compared with that observed in polar crystals. (6) The 5 μ band due to the octaves of the superlattice frequencies is about as strong or even stronger than the 8 μ band, in which they appear as fundamentals, instead of being much weaker as is usually the case with overtone and combination frequencies in crystals. As remarked above, according to the ordinary selection rules, the superlattice frequencies should be inactive in infra-red absorption as fundamentals. The facts recited above indicate that the activity actually observed is connected with the activity of the 1332 cm.$^{-1}$ vibration and is in the nature of a resonance effect.

5. Interpretation of Results. The 5 μ Band

As was mentioned in the previous section, an application of the principles of group theory to a superlattice having twice the linear dimensions of the unit cell (eight times the volume) leads in the case of diamond to the result that the atomic vibration spectrum of this crystal should exhibit eight distinct monochromatic frequencies. Of these, the mode of highest frequency (1332 cm.$^{-1}$) corresponds to the triply degenerate vibration of the two Bravais lattices of carbon atoms with respect to each other. The other seven frequencies which form the superlattice vibrations, represent oscillations of the layers of carbon atoms parallel to the faces of the octahedron or the cube occurring normal or tangential to these planes, with the phase reversed at each successive equivalent layer. By the nature of the case, such oscillations should be inactive in the infra-red absorption as fundamentals under the ordinary selection rules. But owing to anharmonicity the octaves of these frequencies should be capable of appearing in infra-red absorption. Besides the octaves, various combinations of these frequencies would also be active in infra-red absorption.

A detailed exploration of the infra-red absorption band exhibited by diamond in the regions of wavelengths between 4 μ and 5 μ was made by Robertson, Fox and Martin, using a concave grating of one metre focus of echelette type in conjunction with a prismatic instrument. The investigation showed that the band had an observable fine structure; indeed a whole series of sharply defined peaks of absorption maxima was noticed, the positions of which were capable of exact measurement within a few wave-numbers. As Robertson, Fox and Martin have catalogued only four of the

most prominent absorption maxima, careful measurements of the wavelengths and frequencies of all the absorption peaks and kinks made from their published absorption curve are reproduced in Table V.

TABLE V

Infra-Red Absorption Maxima in the 5 μ Region

Description	Wavelength	Wavenumber	Probable Assignment	
	μ	cm.$^{-1}$	cm.$^{-1}$	
Kink ..	5·230	1912	2 × 565 + 784	$2M_2 + H_2$
Peak ..	5·172	1933	784 + 1149	$H_2 + H_1$
Kink ..	5·126	1951	1170 + 784 ?	
$B\beta_2$ Peak ..	5·061	1976		
Peak ..	5·009	1996	1208 + 784	
$B\beta_1$ Peak ..	4·931	2028	2 × 1013	$2K_1$
Kink ..	4·885	2047		
Kink ..	4·835	2068	784 + 1284	$H_2 + M_1$
Peak ..	4·763	2099	1013 + 1088	$K_1 + K_3$
Peak ..	4·721	2118	784 + 1332	$H_2 + F_2$
Kink ..	4·673	2140	2 × 565 + 1013	$2M_2 + K_1$
Ba_2 Peak ..	4·608	2170	2 × 1088	$2K_3$
Peak ..	4·578	2184	1170 + 1013 ?	
Ba_1 Peak ..	4·511	2217	2 × 565 + 1088	$2M_2 + K_3$
Kink ..	4·474	2236	1088 + 1149	$K_3 + H_1$
Peak ..	4·392	2277	2 × 565 + 1149	$2M_2 + H_1$
† Broad Peak	4·03	2482	2 × 1248	$2H_4$
† Kink ..	3·89	2573	2 × 1284	$2M_1$
† Centre of Steep Rise	*3·73	*2680	2 × 1332	$2F_2$

* Measurement Approximate.

† These measurements were obtained from the earlier work of Robertson, Fox and Martin (1934).

Probable assignments for most of these frequencies are made in terms of the lattice and superlattice frequencies of diamond. It will be seen that most of the assignments fit within a few wavenumbers with the actual values of the frequencies of the absorption maxima. These results should be considered surprising according to the early theories of crystal dynamics according to which the vibration spectrum of a crystal is essentially continuous. On the other hand they fit in naturally with the ideas regarding crystal dynamics recently put forward by Sir C. V. Raman (1943).

ACKNOWLEDGEMENT

I am greatly indebted to Sir C. V. Raman for the inspiring guidance and kind encouragement he gave me during this research.

Summary

The absorption spectra of four typical diamonds, three of them luminescent and the fourth non-luminescent, have been investigated in the infra-red in the wavelength range $4{\cdot}5\,\mu$ to $13\,\mu$ with a rock-salt prism spectrometer and radiomicrometer. Allowing for reflection, the non-luminescent diamond is found to be completely non-absorbing in the frequency range 770 cm.$^{-1}$ to 1400 cm.$^{-1}$ The luminescent diamonds show a band in this region with a number of absorption maxima whose frequencies may be identified with those of the lattice and superlattice vibrations. The intensity of this band is greatest in the weakly blue-fluorescent diamond, somewhat weaker in the intensely blue-fluorescent diamond and still weaker in the diamond showing both blue and yellow fluorescence. These results are accounted for on the basis of the crystal structure and symmetry of diamond in its various allotropic modifications. The absorption peaks appearing in the region between 1400 to 2700 cm.$^{-1}$ are accounted for as octaves and combinations of the lattice and superlattice frequencies which are allowed by virtue of the anharmonicity of the vibrations. The appearance of the superlattice frequencies in the $8\,\mu$ band is closely associated with the infra-red activity of the fundamental lattice vibration and is in the nature of a resonance effect.

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LOCAL VARIATIONS IN THE PHOTOCONDUCTIVITY OF DIAMOND

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1. Introduction

The important discovery that though diamonds are usually non-conducting, they conduct electricity under ultra-violet irradiation was first made by Gudden and Pohl (1921). These authors noticed that two of their diamonds showed remarkable differences in behaviour, both in respect of the magnitude of the effect as well as its spectral variation. One non-fluorescent crystal which transmitted the ultraviolet spectrum down to λ 2300 was found to be much more photo-conducting than another which was fluorescent and absorbed ultra-violet radiations of lesser wavelength than λ 3000. Later workers, notably Robertson, Fox and Martin (1934) have investigated the problem in detail. An examination of their data indicates that diamonds show a highly diversified behaviour, the photoconductivity ranging from a very high to a very low value, through successive stages. Pant (1944) who first drew attention to this situation studied the photoconductivity of thirty-six cleavage plates of diamond and arranged them in a regular sequence. He found that the photoconductivity is closely correlated with similar variations in other properties of diamond, notably its ultraviolet transparency and the colour and intensity of its luminescence under ultraviolet irradiation.

The present paper describes a new and hitherto unsuspected phenomenon, namely that the photoconducting power of diamond may show large variations over the area of a single specimen. Such variations could have been expected and have actually been found in the present investigation, in cleavage plates of diamond which show variations in ultraviolet transparency over their area (Raman, Rendall, 1944). Surprisingly enough, however, noticeable variations have also been found in a polished cleavage plate which is completely transparent to ultraviolet radiation upto λ 2250 and also to infra-red radiation in the 8 μ region. It appears that these variations are connected with variations in the degree of mosaicity of the crystal which is suggested by the varying nature of the birefringence pattern of the plate in different parts of it as seen between crossed polaroids.

The diamonds examined were all cleavage plates with well polished faces, the thickness ranging from 0·8 mm. to 1·3 mm. To study the photoconducting behaviour of a particular region in one of them, an electric field is applied across that region by means of two pointed metallic electrodes kept pressed on the faces of the plate. Light from a quartz mercury arc passing through a slit 2 mm. wide is focussed by two quartz lenses at the particular region, the width of which was about 1 mm. The current produced is amplified and measured. For studying another region, the diamond is moved parallel to the plane faces till the region to be examined is illuminated. Thus the whole surface of the diamond is surveyed by steps.

2. Some Experimental Details

The diamond is clipped between two crocodile clips with all their teeth removed except the front three, so that the points of contact are quite sharp and defined. The clips are mounted on two brass rods movable along a groove made on an ebonite base. The diamond is illuminated on one side by the light of a quartz mercury lamp as explained above, and by the light of a 500 watt. filament lamp filtered through a red filter on the other side. The voltage to be applied is obtained from a set of 144 dry cells connected in series giving a total of 220 volts, any part of which could be tapped. The current generated is amplified by a D.C. amplifier, constructed before by Ananthakrishnan (1934) and working under 120 volts, the amplified current being measured on a shunted galvanometer. By measuring the change in output current for a known small change in input voltage, the current amplification factor is calculated as 3,500, giving an overall sensitivity of 2×10^{-11} amp. in the input circuit for one division deflection on a scale at one metre from the galvanometer in the output circuit.

Because of the pressure applied by the springs in the clips, good contact was obtained between them and the diamond. This is clear from the fact that all the readings given below are reproducible to 2 mm. of deflection, if proper care is taken to remove any polarisation formed inside the crystal. Applying different voltages obtained from the dry battery set across the diamond and measuring the resultant currents in the output circuit, the exact linearity of amplification was tested. Also, irrespective of the fact whether the points of contact were illuminated or not, the photocurrent was strictly proportional to the area illuminated, thus indicating that no spurious charges were produced at the points of contact. If was found that if the following two precautions were not strictly adhered to, highly erroneous results might be obtained. (1) Before each reading, the diamond was cleaned with benzene to remove any surface impurities, dried in folds of filter-paper

and heated to 150° C. to remove any space charges that might have formed before. (2) The sharp ends of the clips were occasionally cleaned to remove any non-conducting material which might get deposited there.

3. Results

The three diamonds N.C. 115, 82 and 127 give interesting ultraviolet transparency patterns. Rough sketches of the patterns are shown in the accompanying figure, numbered as I *a*, II *a*, III *a* respectively. The shaded regions in the other drawings are the regions illuminated and the points marked are the points of contact between the clips and the diamonds. The voltage applied between the clips is 120 volts. The currents corresponding to the different regions are tabulated in Table I.

Table I

Voltage = 120 V. at 1½ mm. apart

Area studied	N.C. 115		N.C. 82		N.C. 127	
	Deflection	Ph. Current in 10^{-10} amp.	Deflection	Ph. Current in 10^{-10} amp.	Deflection	Ph. Current in 10^{-10} amp.
1	116 mm.	23·2	47	9·4	11	2·2
2	17	3·4	22	4·4	16	3·2
3	12	2·4	8	1·6	15	3·0
4	107	21·4	4·5	0·9	9	1·8
5	27	5·4	6·5	1·3	19	3·8
6	224	44·8	12	2·4	9	1·8
7	147	29·5	2	0·4	7	1·4
8	30	6·0	18	3·6		
9	35	7·0	5·5	1·1		
10	5·5	1·1	3·0	0·6		
11	4·0	0·8	4·0	0·8		
12	4·0	0·8	4·0	0·8		
13	5·5	1·1	5·5	1·1		
14	11·5	2·3	4·0	0·8		
15	2·0	0·4	3·5	0·7		
16	90	18	7·5	1·5		

Diamond N.C. 60 which transmitted ultraviolet uniformly throughout the surface was then studied. A voltage of 1000 volts obtained by means of a rectifier was applied across the electrodes which were 2·5 mm. apart. The results are given in Table II. Though variations were not expected, Table II *a* corresponding to Fig. IV *b* clearly shows variations and hence a more thorough study by applying the field parallel to the shorter edge and moving the diamond mm. by mm. along the longer edge, was made. The regions are numbered in Fig. IV *c* and the results given in Table II *b*. A sketch of the birefringence of the diamond as seen between crossed polaroids is given in Fig. IV *a*.

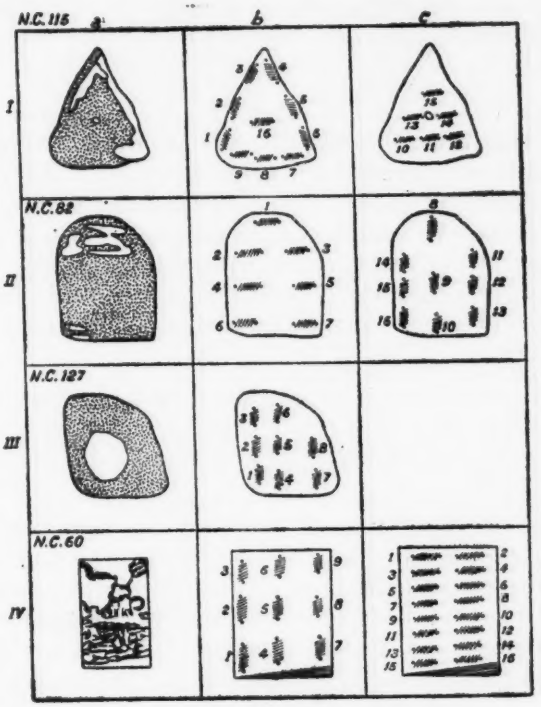

TABLE II

P.D. between electrodes 2·5 mm. apart = 1000 volts

	(*a*) See Fig. IV *b*		(*b*) See Fig. IV *c*	
Area studied	Deflection mm.	Photo Curr. in 10^{-10} amp.	Deflection mm.	Photo Curr. in 10^{-10} amp.
1	57	11·4	29	5·8
2	43	8·6	44	8·8
3	30	6·0	25	5·0
4	50	10·0	28	5·6
5	55	11·0	36	7·2
6	40	8·0	30	6·0
7	64	12·8	38	7·6
8	50	10·0	50	10·0
9	47	9·4	31	6·2
10			50	10·0
11			42	8·4
12			50	10·0
13			49	9·8
14			45	9·0
15			58	11·6
16			39	7·8

4. Discussion of Results

A comparative study of the ultraviolet transparency patterns and of the variations in the photoconducting behaviour observed in the three diamonds N.C. 115, 82 and 127 shows that the transparent regions are much more photoconducting than the opaque parts. It will be noticed that variations in photoconductivity are large in N.C. 115, rather smaller in N.C. 82 and still less in N.C. 127. The behaviour of these diamonds in respect of ultraviolet transparency is very similar. Parts of N.C. 115 are highly transparent; N.C. 82 is rather imperfectly transparent in parts. In N.C. 127 the central region is only slightly more transparent than the margin which is completely opaque, a long exposure being found necessary to bring out the difference.

In N.C. 60, a study of the birefringence pattern in relation to the values of photoconductivity given in Table II reveals that the effect is greatest in regions where the birefringence pattern consists of fine streaks and least where it is full of patches.

Any theory of the photoconductivity of diamond must necessarily consider the following factors; (1) the power of the activating ultraviolet radiation to penetrate into the crystal; (2) its power to set free electrons from the crystal lattice; and (3) the ability of the electrons so set free to move sufficient distances to transport a charge. The striking dependence of photoconductivity on ultraviolet transparency is presumably explicable on the basis of the first factor itself. The variations in photoconductivity shown by the different regions of N.C. 60 indicate, however, that the other two factors may also be variable and that such variations have also to be considered.

N.C. 60, as mentioned above, shows variations in the nature of birefringence over its surface. But birefringence as such is a macroscopic phenomenon and is not necessarily an indication of any variations in the fine structure of the crystal. However, as has been shown by G. N. Ramachandran in another paper appearing in the present symposium, the X-ray topographs of such diamonds exhibit a close relationship to the birefringence patterns. Since the varying intensity of X-ray reflection arises from mosaicity of crystal structure, variations in the nature of the birefringence pattern may be indicative of variations in the degree of mosaicity. At any rate, it is not improbable that over the region in N.C. 60 where the birefringence, pattern is streaky, the mosaicity of structure may be greater, thereby giving rise to a larger number of photoelectrically active centres. *Per contra*, where the birefringence is patchy, the mosaicity may be less and consequently the

number of active centres may also be less. Whether this is the correct explanation of the differences in photoconductivity or whether the variations are due to differences in the free paths of electrons in different parts in the plate, can only be established by further investigations.

In conclusion, the author wishes to express his deep sense of gratitude to Sir C. V. Raman for the great interest he has taken in this work and for the constant encouragement given by him during the course of the work.

Summary

Three cleavage plates of diamond showing variations of ultraviolet transparency over their area have been studied with respect to their photoconducting behaviour. It is found that the transparent regions are more photoconducting than the opaque, the actual value of the photocurrent in a region depending on the degree of ultraviolet transparency.

A fourth plate of diamond which was completely transparent to the ultraviolet region above λ 2250 and also to the 8 μ infra-red region throughout its area, also showed variations of photoconductivity. It is suggested that such variations may arise from a variation in the degree of the mosaicity of the crystal structure in different parts of the plate and consequent differences in the number of active centres from which electrons could be released by the incident radiation.

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GEOMETRIC PATTERNS OF FLUORESCENCE IN DIAMOND

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1. Introduction

Working with the polished cleavage plates of diamond in his collection, Sir C. V. Raman (1943) discovered that while several of them show a more or less uniform blue fluorescence under ultraviolet irradiation, others exhibit geometric patterns of fluorescent light with a varying intensity and in some cases also a varying colour over the area of the plate. A detailed study of the phenomenon (Raman, 1944) showed clearly that there are two distinct types of luminescence with different characters designated respectively as "blue" and as "yellow", and that the pattern observed in any particular diamond might be of one or the other description, or of both simultaneously. The "blue" and "yellow" patterns in a diamond might have entirely different configurations, thereby indicating that they have different origins. The geometry of the patterns is clearly related to the crystal structure, a circumstance which indicates that the phenomenon is characteristic of diamond and not a consequence of impurities present in it. This conclusion is reinforced by the fact that cleavage plates showing such patterns also show variations over their area of other physical properties, *viz.*, transparency in the ultraviolet region of the spectrum (Sunanda Bai, 1944 *a*), in the visible spectrum (Anna Mani, 1945), in the infra-red (8 μ) region (Ramanathan, 1946), of the X-ray reflection intensities (Ramachandran, 1944), and of photoconductivity (Achyutan, 1946). In the earlier symposium, photographs were reproduced showing for numerous plates, their luminescence patterns (Sunanda Bai, 1944 *b*), their ultraviolet transparency patterns (Rendall, 1944), their X-ray topographs (Ramachandran, *loc. cit.*) and their birefringence patterns (Raman and Rendall, 1944), and these exhibited highly significant resemblances and differences.

In the present study, considerable improvements have been effected in the technique of photographing the luminescence patterns and in presenting them for detailed scrutiny. As was remarked by Sunanda Bai herself (*loc. cit.*) in her paper on these patterns, a correct rendering of them would only

be possible if the "blue" and "yellow" types of luminescence were separately photographed by the use of appropriate light filters. This has been done in the present investigation, and by attention to various details, *viz.*, critical focussing, adequate magnification and suitable photographic exposures, a notable improvement has been made in recording the details visible in these patterns. In the earlier symposium, illustrations of the different patterns for the same diamonds appeared dispersed over several separate papers, and except in a very few cases it was not easy for the reader to compare them in detail. This defect has been remedied in the present study. Four different patterns, *viz.*, those of the blue luminescence, of the yellow luminescence, of the ultraviolet transparency and of the birefringence have been photographed for each of 19 different cleavage plates of diamond, and these are presented in juxtaposition in the Plates accompanying this paper. All the four patterns have precisely the same magnification and also the identical setting, thereby making it easy for the reader to compare them in detail. The present paper makes an advance over the previous work also in respect of the material studied. 10 out of the 19 diamonds studied are new additions to Sir C. V. Raman's collection. 8 of them are cleavage plates of the smallest available thickness. The confusion which arises from the overlapping of the patterns at different depths which are not completely in register is minimised by the use of such plates. Thin plates naturally require more intense illumination and longer exposures to yield satisfactory pictures. But the extra effort has been fully justified by the results.

2. General Nature of the Patterns

The correlations which exist between luminescence, ultra-violet transparency and birefringence have already been stated by Sir C. V. Raman in his paper (1944) quoted above. They may usefully be reproduced here.

(*a*) A blue-luminescent diamond is invariably of the ultraviolet opaque type, but the opacity diminishes with increasing intensity of luminescence.

(*b*) Non-luminescent diamonds are invariably of the ultraviolet transparent type.

(*c*) The diamonds which exhibit an yellowish-green luminescence are of the intermediate type, in other words, are neither perfectly transparent nor perfectly opaque to the λ 2536 radiations.

(*d*) The foregoing statements are also valid in respect of the individual areas in a cleavage plate which exhibit a luminescence pattern.

(*e*) Diamond may be perfectly isotropic and strain-free; it is then invariably of the blue-luminescent type.

(*f*) Non-luminescent diamond exhibits a characteristic and readily recognisable type of birefringence, consisting of closely-spaced parallel streaks running in several directions through the crystal.

(*g*) Diamond exhibiting the yellowish-green luminescence invariably shows a characteristic type of structural birefringence, consisting of parallel dark and bright bands, usually rather wider apart than those shown by non-luminescent diamonds.

(*h*) Diamond in which the blue-luminescent and non-luminescent types, or the blue-luminescent and the yellowish-green luminescent types are simultaneously present invariably shows structural birefringence.

The reader can easily test the correctness of the foregoing statements for himself by a careful study of the Plates accompanying this paper. The Plates also serve to illustrate the geometric nature of the patterns and the variety of forms which they exhibit, *viz.*, parallel bands, triangles, hexagons, irregular polygons, and spirals. The present investigation also brings into relief the striking differences in geometric configuration or intensity distribution or both, of the "blue" and the "yellow" luminescence patterns. The variations in the properties of diamond exhibited in these patterns have been explained by Sir C. V. Raman as due to the existence of different allotropic modifications, *viz.*, the positive and negative tetrahedral forms designated as Td I and Td II, and the two octahedral forms designated as Oh I and Oh II. Interpenetration of these modifications gives rise to a wide diversity in behaviour. So far as luminescence is concerned, we may again quote here from his paper on the subject.

(*a*) Diamonds with tetrahedral symmetry of structure are, in general, blue-luminescent.

(*b*) Diamonds with octahedral symmetry of structure are non-luminescent.

(*c*) Diamonds in which the tetrahedral and octahedral types of structure are intimately mixed exhibit the yellowish-green type of luminescence.

Attention may here be drawn to the interesting fact that has emerged from the present studies, *viz.*, that the interpenetration of the positive and negative tetrahedral forms gives rise to blue luminescence which may take the shape of parallel bands, straight or curved, as the case may be. The configurations of these bands may be the same or different or partly the same

and partly different from the banding of the yellow luminescence. Instances of such behaviour are furnished by the various diamonds here studied. N.C. 151 in Plate XVII is a particular interesting case showing parallel bands of blue luminescence and of yellow luminescence running in completely different directions.

3. The Diamonds Studied

B1, B2, B3, B4 are large cleavage plates of diamond, each about 5 carats in weight and about 1·5 millimetres thick. The pictures in their case have been magnified only about 2 diameters. All the other cleavage plates are relatively small in size, and their photographs have been magnified from 3 to 10 diameters as necessary in each case. N.C. 151, N.C. 152, N.C. 153, N.C. 154, N.C. 155, N.C. 156, N.C. 159 and N.C. 160 are small thin plates. N.C. 80, N.C. 82, N.C. 100, N.C. 108, N.C. 110, N.C. 111, N.C. 113, N.C. 114 and N.C. 115 were figured in the earlier symposium, but they have been examined afresh for the reasons already explained. N.C. 175 is a new acquisition showing some remarkable features in its patterns.

4. Experimental Technique

Luminescence.—The photographic filters used in the investigation were prepared by the author from suitable dyestuffs in the laboratory by staining a thin film of gelatine with them. An unexposed photographic plate was fixed in a hypo bath and thus all the silver salts were removed from it. In this way a thin clear gelatine film on a glass plate was obtained. To stain the gelatine with the dye, the plate was placed in a flat dish containing an aqueous solution of the dyestuff. The plate was then removed and dried in a dust proof chamber. The filter was then bound with a clean glass plate so that the dyed gelatine was protected from being scratched. Two such filters were prepared, such that one of them transmitted the blue luminescence and cut off the yellow one, while the other cut off the blue luminescence and transmitted the yellow one. Both of them transmitted the red beyond 6000 Å.U., but this did not matter.

The source of light employed for the thicker plates was a carbon arc run at 220 volts with about 8 amperes current. The light of the arc, after passing through a water cell and a filter of Wood's glass is focussed by a short focus lens on to a quartz plate. The diamond was stuck on the quartz plate. The inclination of this plate to the incident beam was so adjusted as to secure a uniform irradiation of the diamond. The diamond should be mounted in such a way that no reflections at the bevelled edges of the crystal are seen through the camera lens. A rectangular glass cell containing a concentrated solution of sodium nitrite was placed in front of the camera

lens. This served as a complementary filter cutting out all the ultraviolet rays transmitted by the Wood's glass. The colour filter for isolating the blue or the yellow luminescence as desired was introduced in front of the camera lens. The camera was fitted with a Zeiss Sonar lens of 5 cm. focus. The luminescence pattern under suitable magnification was very carefully focussed on the photographic plate. Very fast Ilford H.P. 3 plates were used for obtaining the photographs, the time of exposure being varied according to the nature of luminescence. The blue luminescence patterns were obtained with exposures ranging from 15 minutes to 1 hour, but the yellow luminescence required longer exposures ranging from two hours to six hours.

For the thinner plates, sunlight and much longer exposures were employed, other details being the same.

Ultraviolet Transparency.—The procedure which has been developed and found to be simple and successful for the observation of the ultraviolet transparency patterns of diamond is based upon the use of the extremely intense radiation of wavelength 2536 Å.U. furnished by a water-cooled, magnet-deflected mercury arc in quartz. An image of the arc formed by this radiation is thrown on a plate of uranium glass and is made visible by the intense fluorescence of the latter. If a piece of diamond is stuck on the front surface of the uranium glass, its behaviour in respect of transmission through it of the 2536 Å.U. radiation is immediately rendered evident by its screening effect on the fluorescence of the uranium glass. The luminescence of the diamond itself excited by the 2536 Å.U. is of negligible intensity. As the 2536 Å.U. radiation penetrates very little into the glass, the fluorescence seen on its surface is an accurate representation of the variations of transparency of the diamond to that radiation. Provided the plate of diamond is not very thick and it is in close contact with the uranium glass plate, all the details of the transparency patterns are shown up very clearly.

In this connection it should be pointed out that though the mercury arc in quartz when water-cooled and magnet-deflected predominantly gives the 2536 Å.U. radiations, these are accompanied by numerous other radiations of both longer and shorter wavelengths. Since diamond is transparent in every case to radiation of greater wavelengths than 3000 Å.U., and since the latter also could excite the visible fluorescence of the uranyl glass, it is essential for the success of the method that they are eliminated when forming the image of the mercury arc on the uranium glass. This is readily accomplished using an optical train composed of a quartz lens, a constant deviation quartz prism and a second quartz lens to form a mono-

chromatic image of the arc on the uranium glass. Even with this arrangement there is some parasitic illumination due to other radiations scattered at the surface of the lens and the prism and reaching the plate of uranium glass. This, however, gives no trouble, provided the plate is viewed by the fluorescent light alone in a slightly oblique direction and not by the parasitic light coming directly through it. The success and efficiency of the method is entirely due to the extremely great intensity of the 2536 A.U. radiation emitted by the quartz mercury arc under the conditions stated already, in comparison with all such disturbing factors.

The ultraviolet transparency pattern as made visible in the manner explained above can be readily photographed using a short focus camera lens and Ilford Selochrome plates. Many diamonds appear at first quite opaque but when long exposures are given, the photographs exhibit faint patches where the 2536 radiations are weakly transmitted. Careful focussing is needed to bring out the details of the pattern with the maximum of clearness.

Birefringence.—The source of illumination used was a tungsten filament 100 watts, 220 volts lamp enclosed in a box with an aperture. Two polaroids were supported by platforms just above the aperture, the distance between them being 10 cm. The cleavage-plate of diamond under investigation was introduced between the polaroids supported on a strain-free glass plate and could be set in any desired orientation. The polaroids were mounted on circularly divided supports, so that they could be rotated with respect to each other. The birefringence pattern as seen through the crossed polaroids was photographed by using an achromatic camera objective of 5 cm. focus. Ilford Selochrome plates were used for photographing the patterns, the time of exposure depending on the particular case.

The nature of the pattern exhibited by the birefringence of diamond between crossed polaroids was in general found to vary in a remarkable manner when the setting of the diamond in its own plane was altered. The pattern observed repeated itself four times in each complete revolution of the diamond in its own plane while in intermediate positions it was, in general, different. The alterations produced in the birefringence pattern by rotating the diamond, however, were not usually the same at all parts of the diamond, thereby showing clearly that the axes of the birefringence varied from place to place. Photographs of the birefringence patterns different from each other could therefore be obtained by merely setting the diamond in different orientations with reference to the crossed polaroids. At least two such photographs were obtained for each diamond. Only one of them, however,

has been reproduced in the accompanying plates, being that which showed the pattern most clearly in all the different parts of the plate.

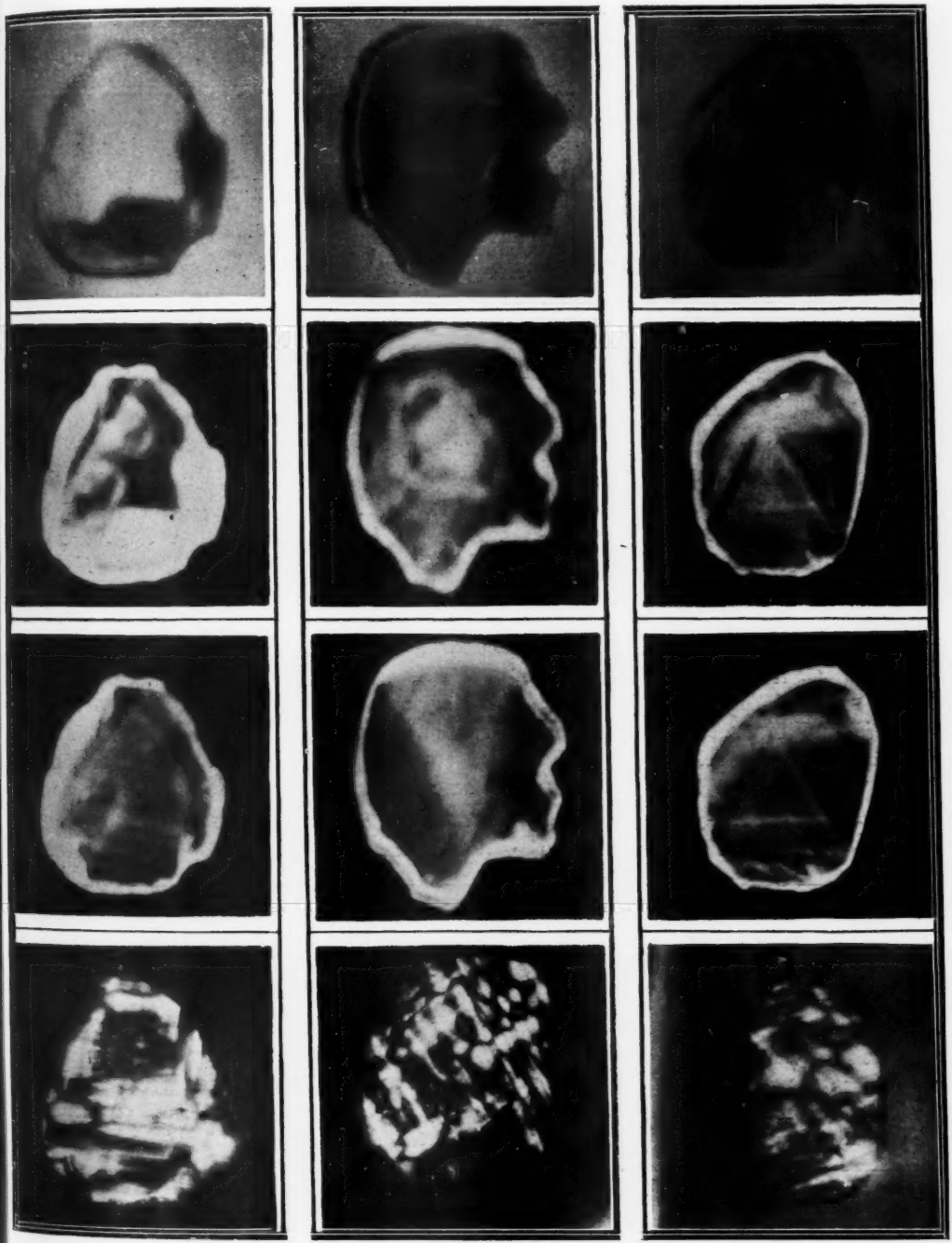
5. Description of the Plates

The pictures marked B1, B2, B3 and B4 in Plate XX are the birefringence patterns of these octahedral cleavage plates and have been reproduced in view of their remarkable hexagonal forms, the lines evidently following the intersections of the other octahedral planes in the crystal with the plane of the cleavage plate. All of them are blue-luminescent diamonds, and being also pretty thick are practically opaque to the λ 2536 radiations. Their luminescence patterns show a set of diffuse hexagons, but as they are not very distinct except in the case of one of them B1, the patterns of B2, B3 and B4 have not been reproduced with the present paper.

In all cases, the four patterns of each diamond have been set above each other as described in the explanation of the plates (see below) at the end of the paper. The photographs have all been reproduced as positives. Comparing them with each other, various resemblances and differences are noticed. A very common and striking feature is that areas which appear as bright in the blue luminescence are reproduced as dark areas in the ultraviolet transmission. This, of course, is because blue-luminescent diamond is ultraviolet opaque. The converse feature, *viz.*, that areas which appear bright in ultraviolet transmission are dark areas in blue luminescence is also noticed, but it is not quite so common nor always so striking. It is explained by the fact that diamond which is completely ultraviolet transparent is non-luminescent, while diamond which is yellow-luminescent is partially transparent to the ultraviolet rays. Cases of both kinds occur, the latter more frequently, the effect being then naturally less conspicuous. There is often but little in common between the features observed in the blue luminescence and the birefringence patterns. This is because blue-luminescent diamond is inherently non-birefringent. On the other hand, striking resemblances are observed between the yellow luminescence and the birefringence patterns. This is because yellow luminescent diamond is laminated in structure and is therefore necessarily birefringent. In some cases, however, the blue and yellow luminescence patterns resemble each other and in such cases both exhibit features analogous to those seen in the birefringence patterns.

In conclusion, the author wishes to express his sincere gratitude to Sir C. V. Raman for his kind interest and guidance.

NC 159 NC 153 NC 160



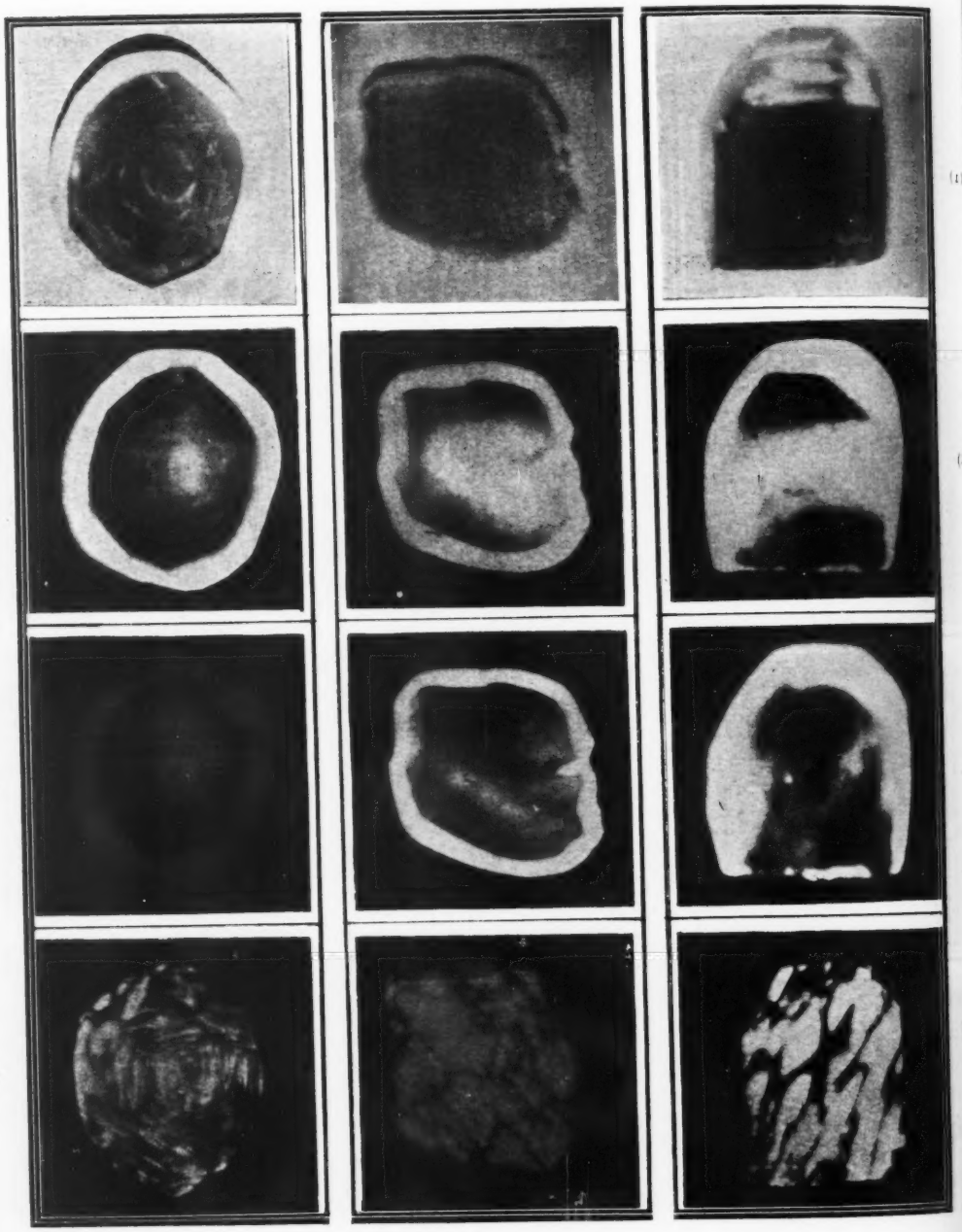
(a)

(b)

(c)

(d)

NC 108 NC 152 NC 82



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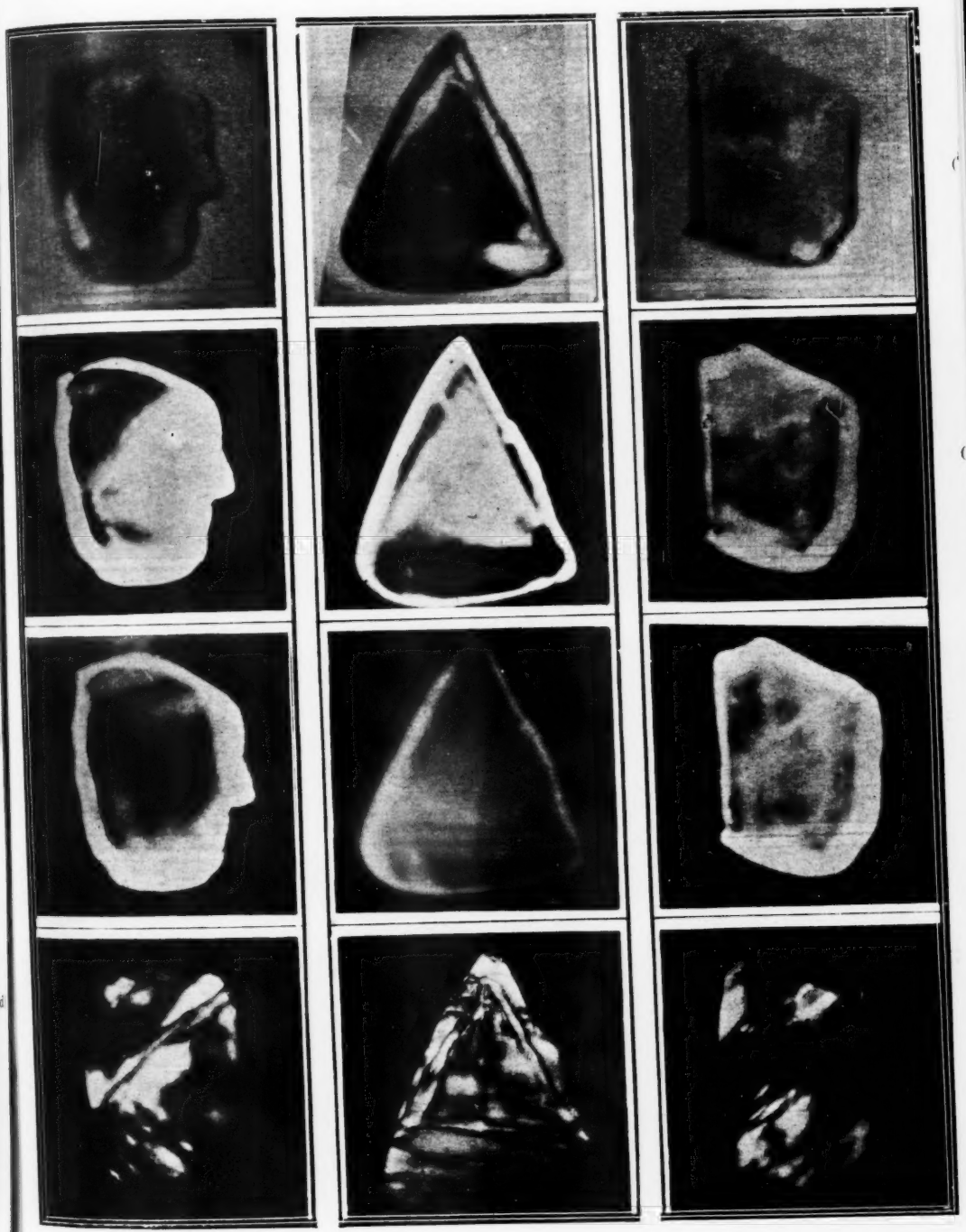

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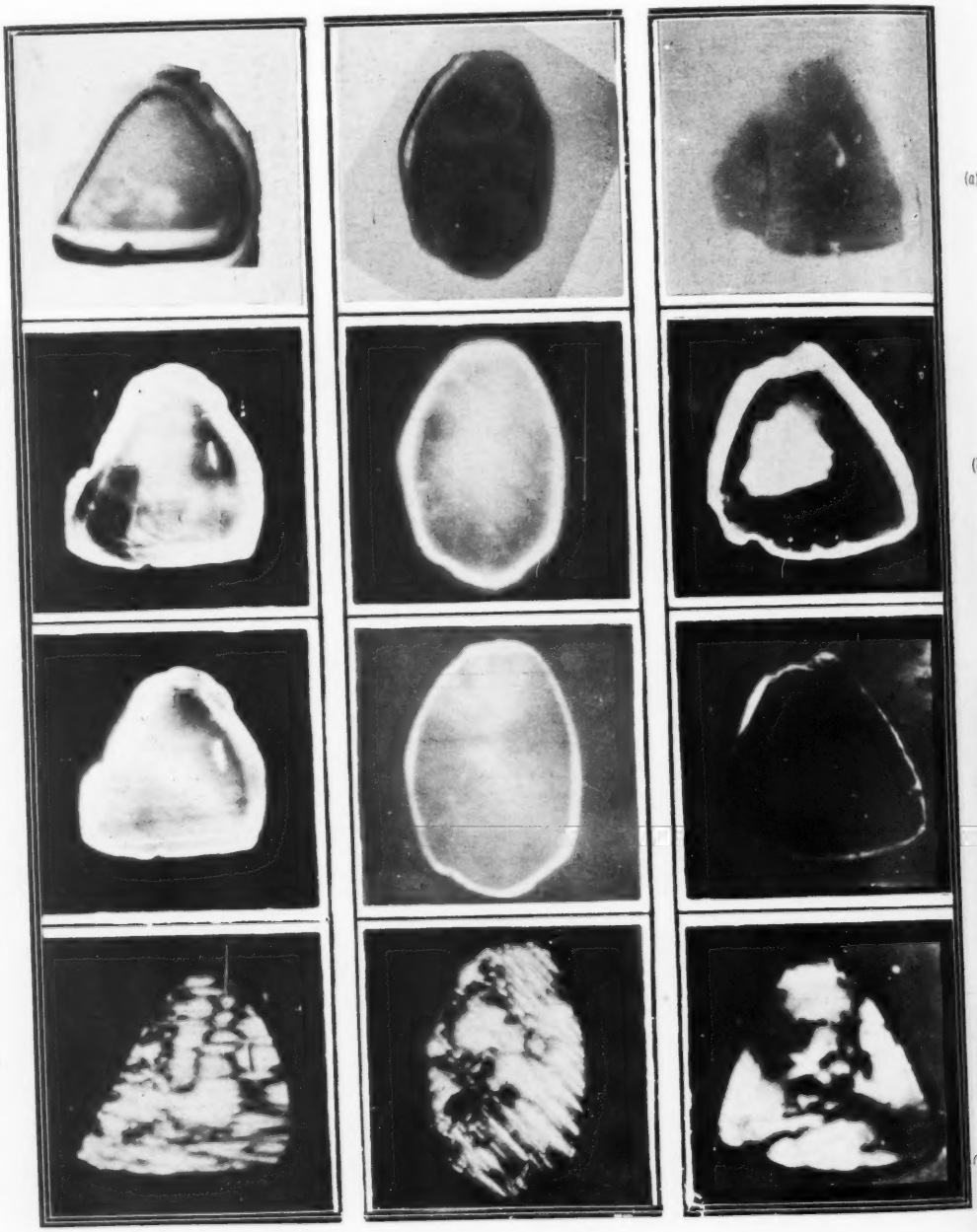
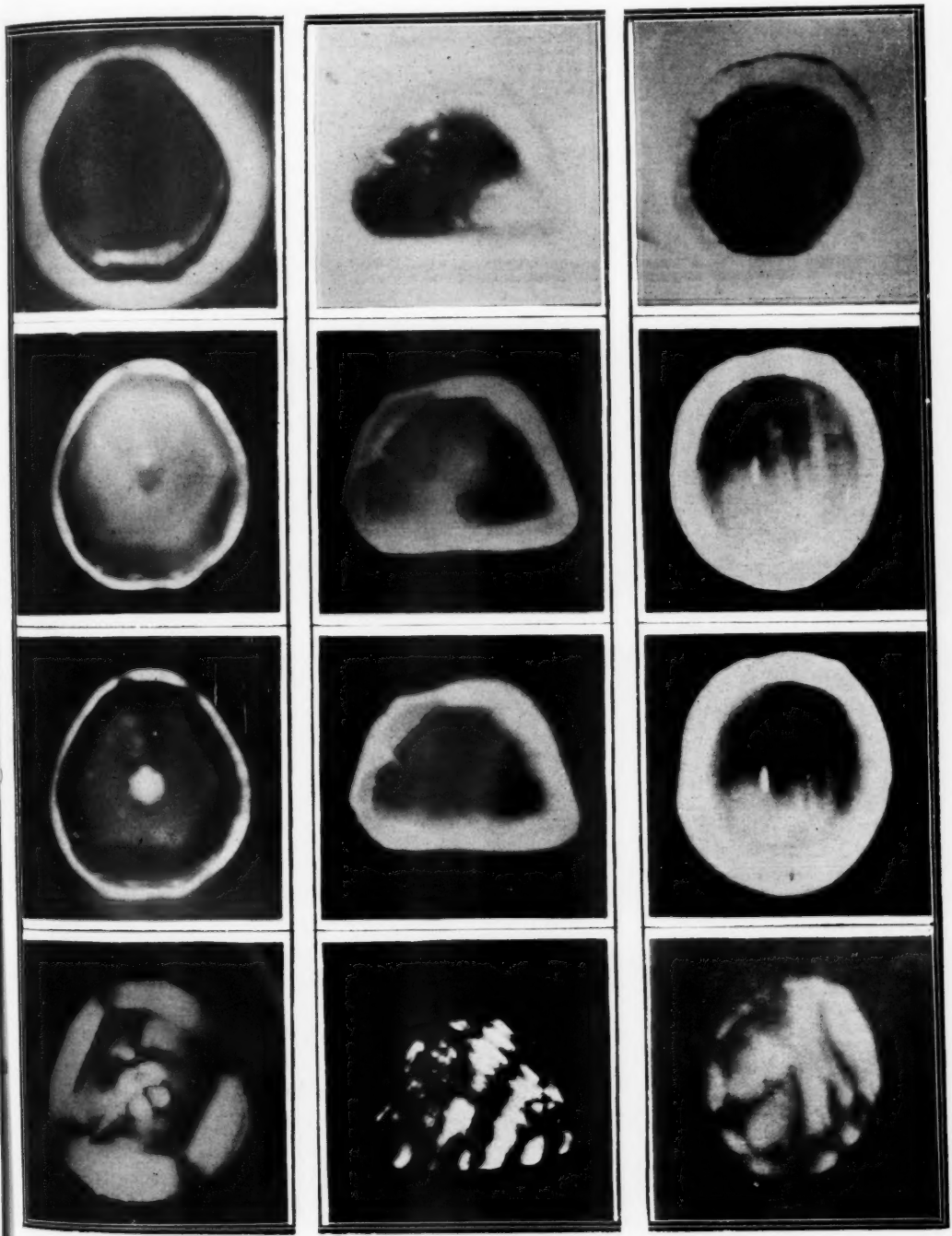


B 1 NC 111 NC 80



(a) (b) (c) (d)

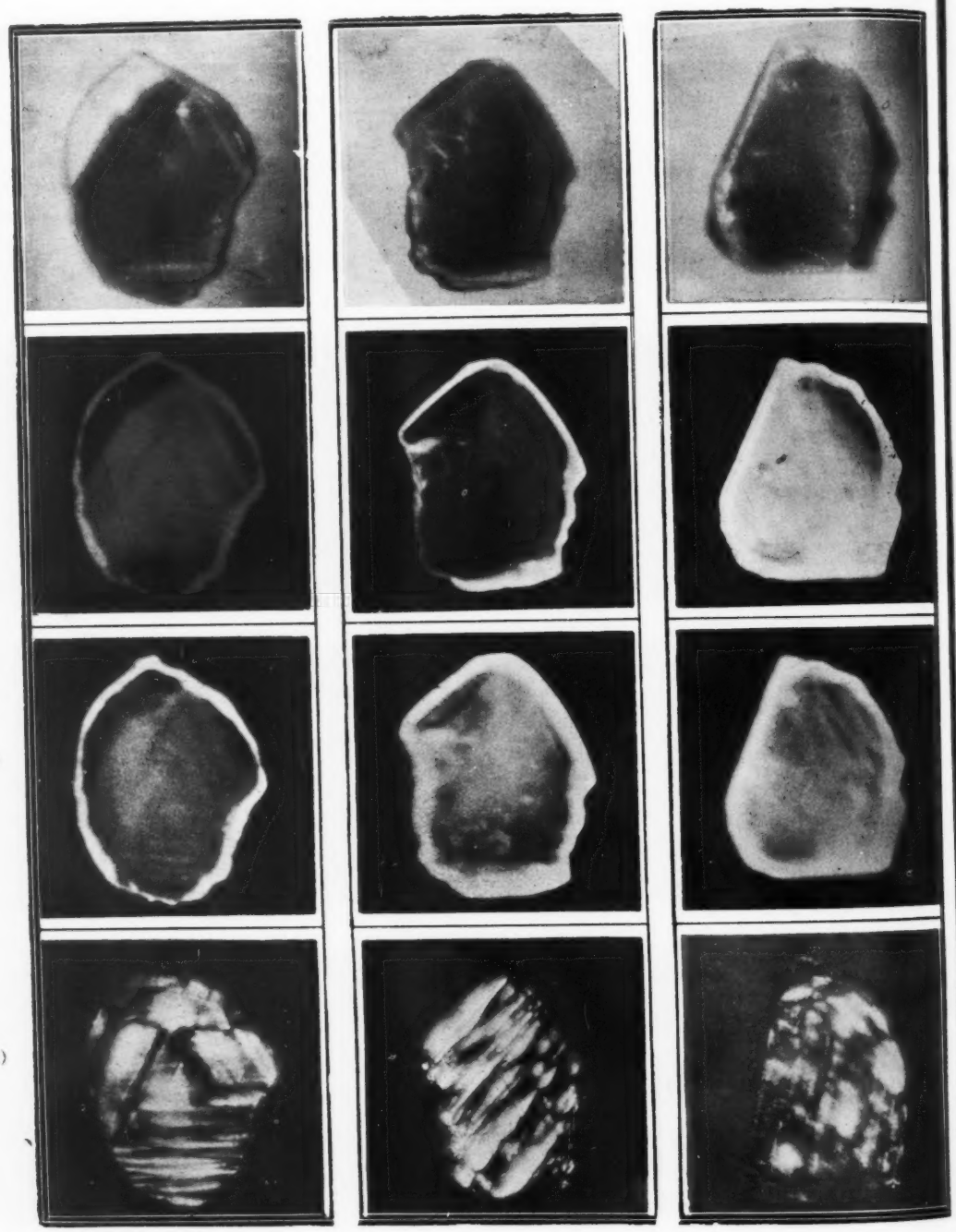
NC 156 NC 155 NC 154

(a)

(b)

(c)

(d)



N C 175

SUMMARY

The blue and yellow patterns of luminescence exhibited by 19 cleavage plates of diamond have been photographed separately using appropriate light filters, and are reproduced along with the patterns of transparency of the same plates to the λ 2536 radiation of the mercury arc and their birefringence patterns. Study and intercomparison of the patterns enables the correlations between luminescence, ultraviolet transparency and birefringence to be readily perceived and interpreted with reference to the structure of the crystal. The blue and yellow patterns are often strikingly different. In some cases, they both appear as parallel bands, but running in different directions through the crystal.

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EXPLANATION OF PLATES XIV TO XX

(*a*) Ultraviolet Transparency Pattern.
(*b*) Blue-luminescence Pattern.
(*c*) Yellow-luminescence Pattern.
(*d*) Birefringence Pattern.

Important Note.—In the case of N.C. 151 on Plate XVII, (*b*) is yellow-luminescence and (*c*) is blue-luminescence pattern.

LUMINESCENCE AS "FORBIDDEN" ELECTRONIC TRANSITIONS IN DIAMOND

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(Communicated by Sir C. V. Raman, Kt. F.R.S., N.L.)

1. Introduction

The fluorescence spectrum of all diamonds at the room temperature exhibits an electronic line at 4156 Å, which also occurs in absorption, accompanied by vibrational bands on the longer wavelength side of it (Nayar, 1941). When the diamond is cooled to liquid air temperatures, the electronic line becomes sharp and is resolved into a doublet with a mean wavelength of 4152 Å. The separation of the doublet is variable, depending on the specimen, but is not less than 2 Å or about 12 cm.$^{-1}$ A number of other electronic lines are also observed, of which one at 5032 Å is also accompanied by subsidiary bands (Mani, 1944). This, however, is very weak in blue-luminescing diamonds. In this paper, we shall discuss the nature and origin of the doublet at 4152 Å, which is present in the spectrum of all fluorescing diamonds.

The first question that arises in this connection is "What is the agent which gives rise to luminescence in diamond?" In the past, it has been generally supposed that some chemical impurity present in the diamond is responsible for the fluorescence. As has been, however, shown by Sir C. V. Raman (1944), there are good reasons for believing that this is not the case. Blue fluorescence is a very general and characteristic property of diamond irrespective of its source of origin and especially of the diamonds which are chemically the purest and physically the most perfect. Blue-fluorescing diamonds exhibit little or no birefringence, while the comparatively less common non-luminescent ones show a characteristic laminated structure accompanied by a strain pattern in the polariscope. The X-ray studies made by one of the authors (Ramachandran, 1944, 1946) indicate, in agreement with this, that the non-luminescent diamonds possess a high degree of mosaicity of structure, while the blue-fluorescent ones make a near approach to the ideal of crystal perfection. These considerations, as well as the close relationships observed between luminescence and other physical properties of diamond, make it highly improbable that it is due to extraneous impurities.

On the other hand, one is led to suppose that the electronic transition is really one occurring between levels belonging to the diamond structure itself. There are, however, considerations to show that the transition is ordinarily forbidden, but that it has become allowed under the conditions existing in the fluorescing diamonds. A study of the refractive index and dispersion of both ultraviolet opaque (fluorescing) and ultraviolet transparent (non-fluorescing) diamonds shows that these do not sensibly differ in the two cases (Martens, 1901; Peter, 1923) and that the variation of the refractive index with wavelength can be represented by a formula using two characteristic frequencies lying in the extreme ultraviolet, *viz.*, at 1750 and 1060 Å respectively (Peter, *loc. cit.*). The contribution of the electronic transition at 4152 Å to the dispersion of diamond is negligible, except probably in the close neighbourhood of this wavelength, where no measurements have been made. This means that the probability of the transition is small, which is equivalent to saying that it is ordinarily forbidden.

There are several cases known in which such forbidden transitions occur in crystals giving rise to both fluorescence and absorption. In ruby, for example, the principal lines in fluorescence and absorption have been attributed to transitions between different levels in the normal configuration $3d^3$ of Cr^{+++} (Deutschbein, 1932). As is to be expected, the wave-numbers do not coincide exactly with those deduced from the energy levels of Cr IV, but are quite close to them. Similarly, a large number of lines have been found in absorption in $KCr(SO_4)_2$ of which the sharpest and the most intense can be attributed to some of the forbidden transitions in Cr^{+++} (Spedding and Nutting, 1934). However, a study of the absorption spectra of a large number of chrome alums shows that the wave-numbers of the intense lines in the red vary appreciably with the compound concerned over a range of nearly 300 $cm.^{-1}$ (Kraus and Nutting, 1941). Similar results have also been found with the salts of the rare earth elements. Ellis (1936) has given reasons to believe that the absorption lines observed in these are due to forbidden transitions taking place between low-lying levels belonging to the normal configuration of the atoms. Calculations of the term values of such levels for Tm^{+++} made by Bethe and Spedding (1937) show remarkable agreement with experimental values. These observations suggest that we might reasonably look for a similar transition to explain the fluorescence in the case of diamond also.

2. Electronic Energy Levels in Diamond

In order to obtain an idea of the energy levels in diamond, it is useful to consider the case of the carbon atom and see if there are any levels in it,

transitions between which are ordinarily forbidden. The authors, however, do not wish to suggest that it is the carbon atom which gives rise to fluorescence in diamond. The energy levels in the carbon atom are only brought in as an analogy in order to obtain an idea of where to look for other forbidden transitions, if any.

The normal configuration $2s^2\,2p^2$ of the carbon atom consists of 3 levels, *viz.*, a group of three levels ($^3P_0$, $^3P_1$, $^3P_2$) forming the ground state and two excited levels $^1D_2$ and $^1S_0$. The term values of these levels with respect to the ground state of C II can be obtained from standard tables (Bacher and Goudsmit, 1932). In Fig. 1 (*a*) an energy level diagram is given with the term value of the $^3P_0$ state taken to be zero. The scheme of energy levels is identical with that in a number of other cases where forbidden transitions have been observed, *e.g.*, that of N II, O III and Pb I and that of O I, except for the inversion of the triplet levels of the ground state ^3P. On the analogy of these cases (Bowen, 1936; Mrozowski, 1944), the transitions which might be expected to occur in C I are shown in Fig. 1 (*a*). The lines $^3P_1$–$^1S_0$ and $^3P_2$–$^1S_0$ have been observed in Pb I by Mrozowski (*loc. cit.*). As will be seen from the diagram, these lines in the case of C I have wave-numbers 21632

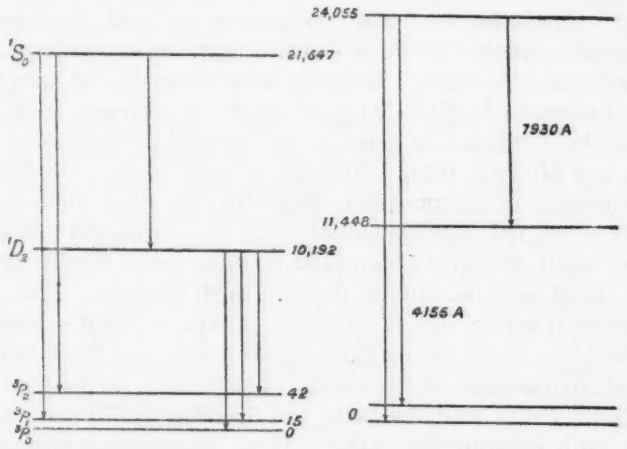

FIG. 1*a*. Energy levels in carbon atom

FIG. 1*b*. Energy levels in diamond

and 21605 respectively, thus forming a doublet with a separation of 27 wave-numbers. As already remarked, the 4152 Å line is also a doublet. One may therefore take the above transitions in carbon to correspond to the 4152 Å line (24077 cm.$^{-1}$) in diamond. It will be noticed that the wave-number of the diamond doublet is 1·114 times that in C I.

Following the analogy, one may expect an intermediate level in diamond corresponding to the $^1D_2$ level in C I. A rough idea of the term value of this level can be obtained if we assume that this also is shifted in the same ratio as the one corresponding to the ^1S level in the carbon atom. The value comes out to be 11340 cm.$^{-1}$ Now, transitions from the ^1D to the ^3P level have been observed in auroral and nebular spectra in the case of N II, O III and O I and in the laboratory in O I and Pb I. Similarly, the transition ^1D–^1S has been found to occur in all the cases, except Pb I where it lies in the infra-red. On the basis of these analogies, one may expect emission lines in diamond at about 7849 Å and 8816 Å. An attempt was therefore made to discover whether any such lines actually occur.

3. Search for the Emission Lines in the Infra-Red

An intensely blue-luminescent diamond (N.C. 67) was used for the purpose and was excited by ultraviolet radiation between 3600 and 4050 Å by using light from a carbon arc filtered through Wood's glass. The red and the infra-red rays transmitted by this glass were cut out by means of a filter of copper sulphate solution. In practice, a round-bottomed flask containing a 10% solution of copper sulphate was used to focus the carbon arc on the diamond. The fluorescence spectrum of the diamond was photographed with a Zeiss 3-prism spectroscope having an aperture of *f*/2·3. With this instrument, the 4152 spectrum could be obtained in 5 seconds, while it required nearly 3 hours to record the infra-red. The spectra were photographed on Kodak extra-rapid infra-red plates which were sensitive upto 8500 Å. (See Plate XXI.)

Actually, it was found that there was a sharp emission line in the fluorescence at 7930 Å. This is clearly shown in Fig. 2 (*a*) at the position indicated by the arrow. The line has also been obtained with another brilliantly blue-fluorescent diamond N.C. 68, whose spectrum is shown in Fig. 2 (*b*). It may be noticed that the line at 7930 Å is actually sharper than the one at 4152 Å indicated by the arrow in Fig. 2 (*d*). This is probably due to the very small dispersion of the spectrograph in the infra-red region. The wavelength of the observed line agrees fairly closely with the expected value of 7849 Å. The other expected line was not recorded, being beyond the limit of sensitiveness of the photographic plate that was available.

It is of interest to examine whether the line at 7930 Å arises from a transition from an upper level to an intermediate level, or whether it is an ordinary transition to the ground level, many examples of which are known. For example Mani (1944) has recorded a number of such electronic lines, occurring both in emission and absorption by diamond, of which those at

5032, 4959, 5359 come out strongly. Two tests can be done to decide the issue. If the transition were one ending in an intermediate level, then it should not occur in absorption and also it should not be emitted unless the exciting light has a wavelength smaller than 4152 Å. The first test, of course, is not very sensitive since it depends on a negative result and may be affected by the fact that a sufficiently long column has not been used for absorption. However, the experiment was tried and it was found that although the absorption line at 4152 Å came out quite clearly, no trace of any absorption could be found in the neighbourhood of 7930 Å.

The second condition for the emission of the infra-red line was also verified. Using the light from a carbon arc filtered through a green filter (which transmitted strongly from 4800 Å to 6000 Å and weakly upto 7000 Å) as the exciting radiation, an exposure of 3 hours only brought out the continuous spectrum in the infra-red weakly. An exposure of 8 hours was required to record the continuous spectrum with about the same intensity as with ultraviolet excitation, but yet the line at 7930 Å was not recorded [see Fig. 2 (*c*)].

These observations strongly support the idea that the transition is one occurring from the higher excited level to an intermediate level. In Fig. 1 (*b*) are shown the energy levels in diamond as calculated from the results reported in this paper.

Our grateful thanks are due to Prof. Sir C. V. Raman for the kind interest that he took in this investigation.

Summary

Arguments are adduced to show that the doublet centred at 4152 Å occurring in the spectrum of all fluorescing diamonds arises from 'forbidden' transitions analogous to the forbidden ^3P–^1S transitions in the spectrum of C I. On the basis of this analogy, fluorescence lines are also expected to occur at about 8816 Å and 7849 Å, analogous to the ^3P–^1D and ^1D–^1S transitions in C I. Of these, the former should also occur in absorption, while the latter should not occur in absorption and should be emitted only if the exciting radiation has a wavelength shorter than 4152 Å. A line has actually been found at 7930 Å, satisfying the latter conditions. The former line could not be recorded being outside the limit of sensitivity of the photographic plate.

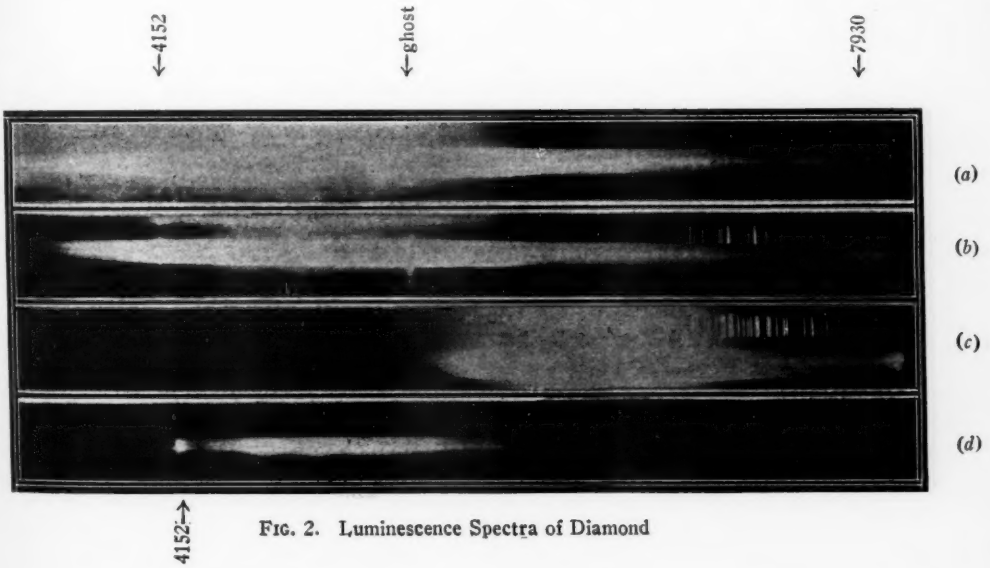

FIG. 2. Luminescence Spectra of Diamond

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PHOSPHORESCENCE PATTERNS IN DIAMOND

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1. Introduction

That some diamonds continue to shine for a while in darkness after exposure to sunlight has long been known and to this phenomenon is applied the term phosphorescence. The brightness of the phosphorescence varies enormously for different diamonds, and this variation is closely related to the strength of emission of visible light under ultraviolet irradiation which in general is known as fluorescence. Brightly phosphorescent diamonds are also brightly fluorescent. However, there is a striking difference in this respect between yellow-fluorescent and blue-fluorescent diamonds (Raman, 1944). The former have a short-lived and scarcely noticeable phosphorescence, while the latter have a bright glow lasting for several minutes. The glow in both types of diamond is greenish yellow. By viewing the diamond through a suitable violet filter, Sir C. V. Raman discovered that for a brief duration of a few seconds, there is blue light accompanying the greenish yellow glow in the case of brightly blue-fluorescent diamonds. But it is the latter that carries most of the energy emitted.

Researches carried out at this Institute (Raman, 1943) have revealed that cleavage plates of diamond often exhibit patterns of fluorescence due to variations in *intensity* of the emitted light from various parts of the plate, and in many cases also variations of *colour*. A detailed investigation of these patterns appears in a paper by G. R. Rendall (1946) in the present symposium. The results of the investigation show that while some diamonds exhibit only blue or yellow fluorescence patterns, others exhibit both of them, and these patterns may be entirely different. Visually it is noticed that cleavage plates which exhibit fluorescence patterns also exhibit phosphorescence paterns, that is, variations of the intensity of the phosphorescence. The object of the present investigations was to photograph such patterns so that they could be studied at leisure and compared in detail with the fluorescence pattterns. The main difficulty in obtaining such patterns is the feebleness of the phenomenon requiring long exposures of more than 50 hours if a phosphoroscope and a camera are used. This has been successfully

overcome by the use of the ingenious method of contact photography suggested by Mr. Hermann Yagoda in a letter to Sir C. V. Raman. The method consists in placing the luminous plate of diamond in direct contact with a sensitive photographic plate in the dark and developing the plate subsequently. The records obtained by this method are presented in this paper. The interesting result has emerged that the yellow phosphorescence emission corresponds to the blue-fluorescence pattern, and that the yellow-fluorescence patterns are not recorded in phosphorescence.

2. Experimental Technique

The technique used in getting the phosphorescence patterns was extremely simple. The best source for exciting the phosphorescence in diamond was found to be sunlight between 10 A.M. and 2 P.M. Sunlight was reflected by a heliostat into a hollow brass tubing fixed in one of the walls of a dark room. Close to this tubing was fixed a lens of aperture 10 cms. and focal length 15 cm. Just in front of the lens was placed a Corning glass filter (3" × 3"), which allows only the ultraviolet light between 3500 and 4000 Å and a little red light above 7000 Å to pass through. The filter also served the useful purpose of cutting off the long-wave radiations which would otherwise heat the diamond. The specimens used in these experiments were cleavage plates of diamond in the collection of Sir C. V. Raman. A hypersensitive panchromatic HP3 plate was kept in readiness inside a darkened chamber. The cleavage plate was held for about a minute in the path of the ultraviolet beam and transferred quickly into the chamber and placed in contact with the sensitive side of the photographic plate. After half an hour, by which time the glow would have practically disappeared for even the most intensely blue-luminescent specimens, the diamond was removed and the photographic plate was developed. A photograph showing great wealth of detail was obtained which may be called the phosphorescent pattern of the diamond, as the prints show at a glance the large variations in the intensity of the evanescent light over the different portions of the same diamond.

In the case of moderately luminescent specimens, the diamonds were placed in contact with a mirror silvered on the front and after excitation dropped along with the mirror on the photographic plate. Thus, a nearly fourfold increase in intensity was obtained as the phosphorescence is doubled up in intensity and the mirror reflects half the phosphorescent light back to the photographic plate. The clarity was not, however, lost as the diamonds were very thin, being rarely more than 1 mm. thick. Another method of obtaining an increase in intensity of the glow—employed especially for big

cleavage plates—was to hold the diamonds at the focus of the ultraviolet light and oscillate the diamonds quickly so that the whole area of the plate is excited uniformly to the maximum possible activation.

One of the possible methods of obtaining the patterns in weakly luminescent diamonds would be to increase the aperture of the lens beyond $f/1{\cdot}5$ used in the experiments. Alternatively, a big concave mirror could be used. But the best method would be to make an arrangement by which the diamonds could be replaced in exactly the same position on the photographic plate. By this method the procedure can be repeated a number of times and each time the exposure need only be for a short time of 2 or 3 minutes, as weakly phosphorescent diamonds have a short-lived glow.

In the case of the intensely blue-fluorescent diamond N.C. 79, it was dropped on the photographic plate half a minute after excitation (Fig. 1 in Plate XXII). Also to show that the glow is mainly yellow and not blue, two more photographs of the glow were obtained by placing two thin gelatin filters respectively between the diamond and the HP3 plate. One of the filters was yellow and transmits wavelengths above 5000 Å, while the other was a violet filter transmitting wavelengths below 5000 A and above 6300 Å. From Fig. 2 in Plate XXII which was obtained with the yellow filter, it is clearly seen that the energy of phosphorescence is almost entirely in the yellow. In the picture obtained with the violet filter (not reproduced), the outline of the diamond was barely visible.

The contact method of photography used in the present investigations might be suitably adapted for taking fluorescent patterns in very feebly fluorescent diamonds. Between the diamond whose pattern is required and the photographic plate a thin cellophane filter, which cuts off the ultraviolet light completely might be placed, ultraviolet light alone being incident on the diamond. Thus the fluorescence pattern alone will be recorded on the photographic plate.

3. Description of the Patterns

The phosphorescence patterns of 12 cleavage plates of diamond of different size and shape are reproduced in Plates XXII and XXIII and the prints have been made of the same size by a suitable enlargement of the negatives. All the diamonds are strongly fluorescent, N.C. 79 being the most intense blue-fluorescent one. The others exhibit varying colours in fluorescence due to mixing of the blue and yellow fluorescence in different proportions. N.C. 110 and N.C. 107 are triangular and N.C. 85 is rod-shaped. N.C. 80 and N.C. 108, are circular, N.C. 106, N.C. 107 and N.C. 114 are very small and thin, while B1, B2, B3 and B4 are large plates.

In most cases, geometric patterns of phosphorescence are obtained. N.C. 110 shows nearly parallel bands, N.C. 80, N.C. 85, N.C. 107 and N.C. 114 exhibit triangles, while B. 1, B. 2, B. 3 and B. 4 show hexagons. N.C. 108 shows an interesting pattern which resembles a spider's web.

4. Comparison of Phosphorescence and Fluorescence Patterns

The comparison of phosphorescence with the fluorescence patterns in the same diamond confirms the observation that brightly blue-fluorescent portions have bright phosphorescence. Thus in the case of purely blue-fluorescent diamonds, both the patterns are exactly analogous. As an example the case of N.C. 79 (old number D. 34) might be cited. The bright blue patch comes out brightly in the phosphorescence patterns also. The fluorescence patterns of this and of N.C. 85 and N.C. 106 (old numbers D. 42 and D. 186 respectively) are given in the paper by Sunanda Bai (1944) in the earlier symposium.

In the case of diamonds showing the mixed type of fluorescence, however, the phosphorescence patterns were compared with the blue and yellow fluorescence patterns recorded separately in the paper by Rendall (1946) which appears in the present symposium. There, the fluorescence patterns of N.C. 80, N.C. 108, N.C. 110, N.C. 114 and B. 1 are represented. The comparison at once reveals that it is the blue and not the yellow pattern that is recorded in the phosphorescence pattern in spite of the fact that the glow is yellow. Striking examples are N.C. 110 and N.C. 114 which show entirely different patterns in the yellow and blue as might be seen in the abovementioned paper. In the yellow fluorescence patterns of these diamonds there are straight parallel bands. In the blue, N.C. 110 exhibits curved bands and a portion at the left bottom is comparatively weakly luminescent. The phosphorescence pattern is identical with the blue-fluorescence pattern. In the blue, N.C. 114 exhibits a patch at the right while the parallel bands appearing in the yellow are entirely missing. The phosphorescence pattern of this diamond shows a bright portion at the right and resembles the blue pattern. However a small portion at the bottom of the bright patch in the blue fluorescence is not recorded in phosphorescence. These observations confirm the finding that yellow fluorescence has only a feeble and short-lived phosphorescence accompanying it. As further confirmation of this, a brightly green-fluorescent diamond was tried and gave an extremely feeble picture showing only the bare outline (not reproduced).

N.C. 80 exhibits nearly the same patterns both in blue and yellow fluorescence and the phosphorescence pattern is similar to both. N.C. 108 has a bright central spot in the blue fluorescence surrounded by a spiral,

while in the yellow the spot is absent. In phosphorescence the central bright spot along with the spiral comes out.

In all the photographs the edges of the diamond come out strongly as they have bright blue-fluorescence and hence strong phosphorescence. In the case of the phosphorescence pattern of B. 1, there is a bright patch in the middle of the hexagon, while in the blue fluorescence pattern this is entirely absent. In the cases of B. 2, B. 3 and B. 4, a larger number of concentric hexagons are obtained in phosphorescence than in fluorescence patterns. In these cases and that of N.C. 114 referred to above, therefore, there are slight departures from the exact identity of the phosphorescence patterns with the blue-fluorescence pattern.

In conclusion the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for suggesting the problem and for the invaluable guidance given during the investigations.

Summary

Phosphorescence patterns in a dozen cleavage plates of diamond revealing the variations in intensity of phosphorescence in different portions of the same diamond have been successfully recorded by the method of contact photography. Comparison of these with the fluorescence patterns in the same diamond shows that the yellow phosphorescence emission corresponds to the blue fluorescence patterns, and that the yellow fluorescence patterns, if present, are not recorded in phosphorescence. Geometric patterns such as parallel bands, triangles, hexagons and spirals have been obtained in many cases.

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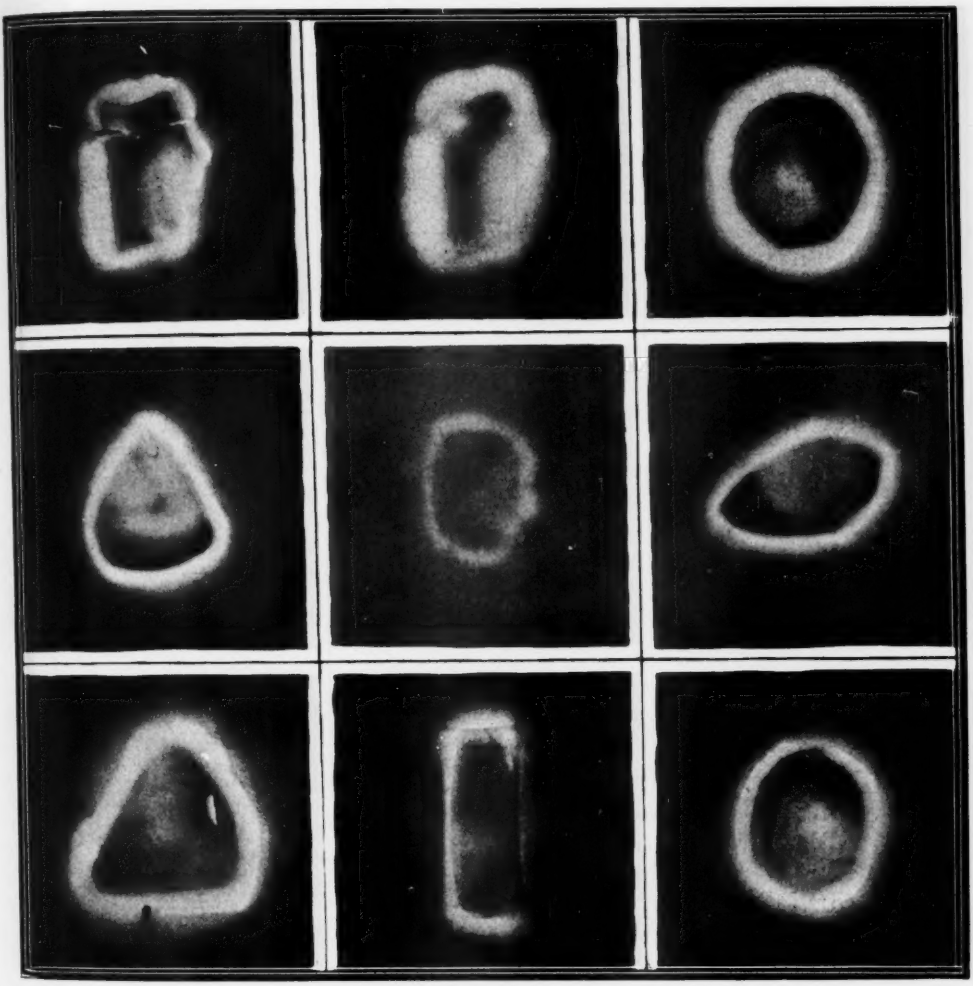
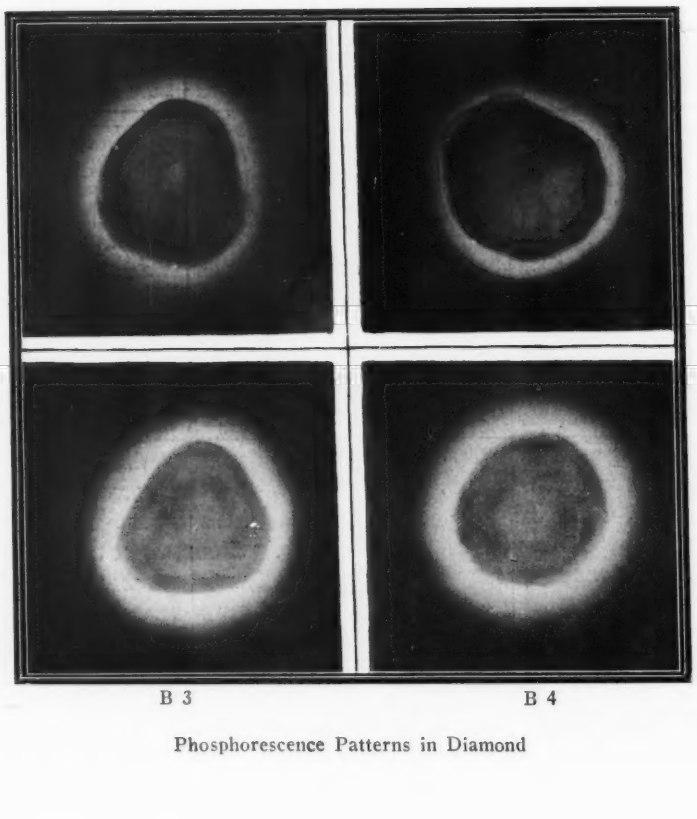


Phosphorescence Patterns in Diamond

N.C. 79	N.C. 79	N.C. 80
N.C. 107	N.C. 114	N.C. 106
N.C. 110	N.C. 85	N.C. 108

B 1 B 2



B 3 B 4

Phosphorescence Patterns in Diamond

THE THERMOLUMINESCENCE OF DIAMOND

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1. Introduction

Some substances have the property of storing up energy under suitable excitation which they later release. The release of energy as visible light at the temperature of excitation is known as phosphorescence. But, even after the afterglow has decayed, the substance may retain some of the stored-up energy which manifests itself as light on heating the substance in darkness. To this phenomenon is applied the term thermoluminescence. That some diamonds exhibit thermoluminescence has long been familiar to several investigators in the past. In the twelfth century, Albertus Magnus by placing the diamond in hot water noticed the glow, while in the seventeenth century, Robert Boyle held a diamond near a flame and observed its glimmering on removing it quickly to a distance. However, there seems to be no recent work on the subject mentioned in the literature. The present paper describes the results of a study of thermoluminescence undertaken by the author, and these are briefly enumerated below.

Fluorescent diamonds, after exposure to ultraviolet of the sun, glow in darkness with a greenish-yellow colour. In the case of brightly blue-fluorescent diamonds, Sir C. V. Raman discovered that for a brief duration of a few seconds, there is blue light accompanying the greenish-yellow glow which lasts for several minutes. On raising the temperature of the diamond to 270° C., the colour of the visible afterglow changes to blue and it is very bright. This thermoluminescence is observed even if the diamond is heated a few days after activation, by which time the ordinary phosphorescence would have completely disappeared. There is the yellow portion also in the blue thermoluminescence, as can be verified by viewing the diamond through an yellow filter. Another important result of the investigation is that the ultraviolet light below 3200 Å is able to excite thermoluminescence more efficiently than ultraviolet between 3500 and 4000 Å, even though the former excites little phosphorescence at room temperature. X-rays are also able to produce a slight activation. The effect of irradiation of the diamond with light of wavelength greater than 4200 Å is to practically remove the activa-

tion in diamonds even at or below room temperature. Green fluorescent diamonds show a weak greenish-yellow thermoluminescence.

2. Phosphorescence

In order to facilitate an understanding of the thermoluminescence, the main facts about the phosphorescence of diamond are briefly stated below. They will be dealt with in greater detail in a separate paper on the subject appearing in the present symposium. The source of light used in the study was sunlight and the arrangement was that described in the paper on phosphorescence patterns also appearing in the present symposium.

Blue-fluorescent Diamonds.—The colour of the light emitted by blue-fluorescent diamonds under the ultraviolet of the sun changes suddenly to greenish yellow when the exciting radiation is cut off. The afterglow can be seen for about half an hour in darkness in the case of the strongly blue-luminescent diamonds. Observation of the diamond through suitable light filters enables us to obtain an idea of the nature of the phosphorescence spectrum. It is found that the glow can be seen with almost undiminished intensity through an yellow filter transmitting above λ 5000 for practically the whole of its duration. On the other hand, through a violet filter cutting off between 4950 and 6300 Å the diamond is visible faintly for a relatively short duration of about 20 seconds. Thus the energy of the phosphorescence is mainly in wavelengths above 5000 Å. This is further confirmed by viewing the diamond through a filter which has its cut-off between λ 5200 and λ 6250. The phosphorescence is then seen more brightly and for a longer duration of a few minutes. On viewing the afterglow through a direct vision spectroscope, the spectrum is found to extend at first on both sides of λ 5000, but in a few seconds the spectrum on the violet side diminishes in intensity relatively to that on the green side. However, the entire spectrum also becomes very feeble and it is not possible to continue its study after the first few seconds. There is no red phosphorescence, as the glow is invisible through a red filter transmitting above 6300 Å. The brightness of the phosphorescence increases with the intensity of the ultraviolet light used. However, a variation of the time of irradiation from one second to several minutes produced no perceptible increase in intensity of the glow, and the time for which the diamond can be perceived through the various filters remains unaltered. The brightness of the glow in different diamonds increases with the intensity of their fluorescence.

One of the diamonds was cooled by immersing it in liquid air contained in a Dewar flask and then irradiated with ultraviolet light. On shutting

off the light, a greenish-yellow glow was detected for 30 seconds, as has already been mentioned in a paper by Nayar (1941).

Green-fluorescent Diamonds.—Green fluorescent diamonds in striking contrast with the blue ones exhibit a faint greenish-yellow glow which lasts for only 40 seconds even in the case of the most brightly fluorescent specimens. As the glow is faint and of short duration, it cannot be examined through filters.

General Remarks.—In the fluorescence spectra of all diamonds, electronic lines at λ 4152 and λ 5032 with their accompanying bands at longer wavelengths are recorded. In blue-fluorescent diamonds the λ 4152 system is strong but the λ 5032 is also recorded in many cases though weakly. In green-fluorescent diamonds, the λ 5032 system is strong but is always accompanied by the λ 4152 system though with relatively much less intensity. On the other hand, the phosphorescence spectra of strongly blue-fluorescing diamonds recorded by Nayar (1941) and Miss Mani (unpublished work) show both the λ 4152 and λ 5032 system with comparable intensity. Their spectrograms were obtained with a time-interval of the order of a fraction of a second between excitation and observation. The visual observations described in the present paper indicate that with longer time-intervals the λ 4152 grows gradually weaker and disappears after a few seconds and that the subsequent phosphorescence consists exclusively of λ 5032 and its accompanying band system. Further experimental work is necessary to confirm this finding and also to investigate how the duration of the phosphorescence of any diamond depends upon the relative and absolute intensities of the λ 4152 and λ 5032 systems as exhibited in its fluorescence.

3. Thermoluminescence

A blue-fluorescent diamond N.C. 67 was activated by exposing it to the ultraviolet light of the sun and was then placed on a hot plate whose temperature was about 100° C. The glow brightened up but the colour remained unaltered. When the temperature of the diamond was raised to 270° C., the glow was very bright and *blue in colour*. However, the diamond could be observed through the yellow filter indicating that the yellow portion must also be accompanying the blue glow. The blue thermoluminescence was perceived for about 10 minutes.

In all the above described experiments, ultraviolet light between 3500 and 4000 Å has been used. To use ultraviolet light below λ 3000, the light from an iron arc was focussed by a quartz lens on the diamond. After shutting off the incident light the diamond showed little phosphorescence.

However, on heating the diamond, bright blue thermoluminescence was observed. When during irradiation, a glass plate was introduced between the diamond and the quartz lens, the intensity of thermoluminescence became extremely small, showing that wavelengths below 3000 Å produce very high activation compared to wavelengths between 3500 and 4000 Å. As a further confirmation of this, the diamond was held close to a water-cooled low-pressure quartz mercury arc and then heated to 270° C. in darkness. A brilliant blue glow was observed.

The diamond N.C. 67 was activated by means of the light of an iron arc and kept in darkness. After 10 days the diamond was heated to 270° C. and a blue glow was observable. Thus some energy can be stored up in the diamond for any length of time. It should be realised, however, that the heating does not produce, but only releases the energy 'frozen in' at room temperature, as the thermoluminescence glow is not persistent at the high temperature like fluorescence, but decays (Pringsheim and Vogel, 1943). Thermoluminescence is nothing but phosphorescence at a high temperature. In support of this view the heated diamond at 270° C. was irradiated with ultraviolet light and on shutting off the light, the phosphorescence was bright blue. P. G. N. Nayar has similarly observed that the phosphorescence at room temperature could be quenched at any stage of its life by immersion in liquid air and the residual part of its life completed on regaining the room temperature.

The effect of X-rays in producing the activation in the diamond was tried. The diamond N.C. 67 was heated for several minutes at 270° C. until no trace of glow was detected and after cooling, it was irradiated by X-rays. It was then again heated to 270° C. in darkness and a faint blue glow appeared which was visible for about a minute.

In the case of a green-fluorescent diamond N.C. 41, a comparatively faint *greenish-yellow* glow was detected for about 10 minutes on heating it to 270° C.

4. The Effect of Red Light

It has been stated above that the activation in N.C. 67 could be retained for several days and released on heating it. The diamond after activation was exposed for about a minute to bright red light of the sun obtained by the use of a red filter, and on heating the diamond subsequently an extremely faint glow was detected. Thus the activation was practically removed. Similarly, when the phosphorescing diamond was exposed for a minute to red light, the brightness of the phosphorescence was much smaller than what it would otherwise have been. A careful study of the effect of red light will

be presented in a later paper. It was found by the use of various filters that any wavelength above 4200 Å was able to remove the activation in diamond. In fact, if the diamond after exposure to focussed ultraviolet light of the sun was taken out into bright daylight, the activation disappeared practically as was verified by heating the diamond subsequently.

5. Discussion

The foregoing experiments have made it clear that there are two distinct types of phosphorescence, one blue and the other yellow. The former is faint and observable only for a short time at and below room temperature, while the latter predominates in the glow and lasts for a long time. At high temperatures, the glow is blue showing that the blue then prodominates. The ultraviolet light below 3000 Å is able to excite thermoluminescence with greater efficiency than the very near ultraviolet, while the converse is true of phosphorescence at room temperature. These facts have to be remembered in presenting any theory of the phosphorescence of diamond.

The blue phosphorescence and thermoluminescence may be identified with the λ 4152 system, while the yellow phosphorescence and thermoluminescence may be identified with the λ 5032 system. However, the diamonds which show the latter system brightly in fluorescence compared to the former, show only feeble greenish-yellow phosphorescence and greenish-yellow thermoluminescence.

In the fluorescence of diamond, principally two electronic lines λ 4152 and λ 5032 are found (Anna Mani, 1944) and as these come out in absorption also, there are three main energy levels, one ground and two upper ones, in diamond. The usual explanation of phosphorescence is based on the idea that there are metastable levels near the upper levels in which some electrons are trapped. Due to the thermal agitation, these slowly leak to the main levels and from there they drop to the ground state emitting light. This view is supported in the case of the after-glow of diamond as both the 4152 and 5032 lines are observed in phosphorescence. There must also, however, be some traps from which the electrons cannot escape at room temperature. On raising the temperature, however, the electrons are enabled to escape from these levels.

In conclusion the author wishes to thank Sir C. V. Raman, Kt., F.R.S., N.L., for suggesting the problem and for the encouragement given during this work.

6. Summary

Blue-fluorescent diamonds show a greenish-yellow glow at room temperature after exposure to ultraviolet light. In this glow, there is also a blue component which however decays more rapidly. On heating to 270° C. the colour of the glow changes to blue and the glow brightens up. This effect, known as thermoluminescence, can be observed even if the diamond is heated a few days after activation. Remarkably enough, radiations below 3000 Å are able to produce an activation greater than that produced by radiations between λ 3500 and λ 4000, even though the former give rise only to slight phosphorescence. Even X-rays are able to produce a slight activation. In the case of the green-fluorescent diamonds, the phosphorescence is feeble and greenish yellow in colour. The thermoluminescence of these diamonds is greenish-yellow and is much fainter than that of blue fluorescent ones. Light of any wavelength greater than λ 4200 is able to remove the activation in both varieties of diamond.

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THE PHOSPHORESCENCE OF DIAMOND

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1. Introduction

A remarkable property of many diamonds is their power to store up energy under ultraviolet irradiation, a portion of which is released as visible light on shutting off the exciting radiation. This phenomenon, known as phosphorescence, has been remarked upon by several early workers like Robert Boyle, Crookes, Becquerel and others. However, the rest of the energy is retained in the diamond even for several days and released as visible light on either heating or more effectively on re-illuminating the diamond with long wavelength radiations even at or below room temperature. The former effect of heating has been dealt with in the paper on thermoluminescence appearing in the present symposium, while the latter is mainly dealt with in this paper. The main facts about phosphorescence already summarised in the paper referred to are also presented here more fully.

Diamonds which show bright blue fluorescence under ultraviolet light exhibit a greenish-yellow afterglow for about 30 minutes in which there is also a blue component during the first few seconds. Sir C. V. Raman discovered this fact by the use of a violet filter and this technique of viewing the diamond through filters has been found extremely useful in studying the effect of re-illumination. The green-fluorescent diamonds show only a feeble phosphorescence. When blue-fluorescent diamonds after exposure to ultraviolet light are re-illuminated with red light and viewed through a filter complementary to the red, a very bright blue flash is observed which dies away in a few minutes. In the case of green-fluorescent diamonds, the flash is green. Both varieties of diamonds on heating lose their activation in the form of thermoluminescence. Ultraviolet light below 3000 Å produces activation several times greater than that produced by radiation between 3500 and 4000 Å. X-rays are also able to produce a slight activation. Any wavelength above 4200 Å is able to remove the activation in diamonds.

2. Phosphorescence

The main facts about the phosphorescence of diamonds have already been stated in the paper on thermoluminescence appearing in the present symposium. As the specimens N.C. 67, N.C. 68, and N.C. 41 have been

used in the study of re-illumination with long wavelength radiations, their phosphorescence is described below. The former two are small brilliants and are intensely blue-fluorescent, while N.C. 41 is a moderately large crystal which is brightly green-fluorescent. N.C. 67 and N.C. 68 after exposure to ultraviolet light of the sun exhibit a greenish yellow glow and the change of colour from the blue fluorescence to greenish yellow phosphorescence is very striking. To find whether any blue phosphorescence is present in the glow, the diamond is viewed through a violet filter having a cut-off between 4950 and 6300 Å; a faint glow is then detected lasting for about 20 seconds. The main bulk of the emitted energy is, however, in the yellow, as the brightness of the glow is practically undiminished by the interposition of an yellow filter transmitting wavelengths greater than 5000 Å. The green-fluorescent diamond shows a faint greenish yellow glow lasting for about 40 seconds which is, however, too faint to be studied with filters.

It is found that the decay of the afterglow in all cases is extremely rapid in the first few seconds. It is proposed to take up the exact nature of the decay in a further communication.

The fluorescence spectra of diamonds taken by Miss Mani (1944) reveal mainly a line at λ 4152 and a system of bands associated with it and also another line at λ 5032 and an accompanying band system. In the phosphorescence spectrum of N.C. 68 taken by Miss Mani (unpublished work), both systems appeared. As the time interval between irradiation and exposure was only a fraction of a second, the violet phosphorescence was present and was recorded as the 4152 system. The green glow may be identified with the 5032 system which presumably has a long lifetime in the phosphorescence of blue-fluorescent diamonds.

3. The Effect of Red Light

In order to follow the effect of re-illumination, it is important to recall the Stokes law of fluorescence. The wavelength of the exciting radiation should be near about or less than the wavelength of fluorescence. Thus red light is unable to excite any visible fluorescence, and similarly green light cannot produce any violet fluorescence.

Blue-Fluorescent Diamonds.—The diamond N.C. 67 is exposed to ultraviolet light of the sun for about a minute and after shutting it off, red light obtained by passing sunlight through a red filter transmitting above 6300 Å is focussed on it. On viewing the diamond through a 3 cm. filter of saturated copper sulphate solution which is complementary to red light, a bright blue flash is observed which decays very rapidly in the beginning and is visible for about four minutes. As red light cannot produce an

fluorescence, the flash is due to the release of the stored-up energy in the diamond by red light. Even though the colour of the flash is blue, it also contains wavelengths from 5000 to 6000 Å. This is shown by the fact that the glow can be observed both through a blue filter of ammoniacal copper sulphate solution transmitting wavelengths less than 4600 Å and through a green filter transmitting 5000 to 6000 Å.

On illuminating the activated diamond with green light (5000 to 6000 Å) of the sun and observing through a complementary violet filter, a bright violet flash is observed for about two seconds, and subsequently there is a persistent faint red colour due to fluorescence produced by the green light. The violet flash is, however, due to the release of activation energy by the green light as is indicated by the decaying of the flash.

The effect of both green light and red light can be noticed even a few days after activation by ultraviolet light. This indicates that the stored-up energy is retained by the diamond and is released by exposure to green light for a sufficient time, since red light has subsequently no effect; also, *vice versa.* If similarly the activated diamond is exposed to blue light (4100 to 5000 Å) for about a minute, any flash occurring during the exposure cannot be observed through a complementary filter owing to the presence of a persistent green and red fluorescence produced by blue light. However, after such exposure, the diamond no longer shows any flash on irradiation with red light, thereby indicating that blue light is able to remove the stored-up energy presumably as a flash. Using a monochromator with sunlight as the source, a preliminary study of the efficiency of different wavelengths in removing the activation in the blue-fluorescent diamond N.C. 68 has been made. Green light near about λ 5500 appears to be the most efficient, but a more thorough examination of the facts will be published later. It is also found that for a given wavelength, the brightness of the flash increases with intensity of the light used while the duration of visibility diminishes, showing that the whole of the stored-up energy is released in a shorter interval of time by a more intense source of light.

The activation in diamond is increased on increasing the intensity of the activating ultra-violet light. However, as in the case of phosphorescence, the time of irradiation need only be a second. Increased exposure times do not result in an observable increase in the intensity of the flash which results from illuminating the diamond with a constant source of red light.

When the radiations from a low pressure quartz mercury arc are used for activation, it was found that the blue flash obtained by subsequent irradiation with red light (above 6800 Å) is much brighter than when the

near ultraviolet between 3500 and 4000 Å is employed for activation. In fact, the blue colour is clearly seen for a few seconds even in the presence of the intense red light in the former case, while a filter of copper sulphate solution has to be used to cut out the red light if the blue flash is to be observed in the latter case. A very large part of the high activation produced by the quartz mercury arc is due to radiations below 3000 Å. This is shown by the fact that when a glass plate which cuts off these wavelengths is interposed between the diamond and the mercury arc, the activation is reduced to a very small fraction of its former strength. It is also found that subsequent exposure to light between 3500 and 4000 Å reduces the large activation produced by radiations below 3000 Å.

During any part of a flash if the illuminating light is cut off, the flash disappears instantaneously as far as the eye can judge. The remaining part of the flash can be completed at any later time by illuminating again with the light.

X-rays are also able to produce a slight activation. This can be verified by removing all previous activation in the diamond by exposure to bright red light for about half an hour and then irradiating it with X-rays for a few seconds. Subsequently, when red light is allowed to fall on the diamond, a feeble blue flash is observed through the copper sulphate filter.

Green-fluorescent Diamonds.—The green fluorescent diamond N.C. 41 behaves in exactly the same way with regard to all the above effects except for the fact that the flash is green as observed through copper sulphate solution and not blue. The major portion of the energy of the flash is hence in the green.

Spectrum of the Flash.—The diamond N.C. 67 after activation by focussing the light of a quartz mercury arc on it with a quartz lens, was placed very close to the slit of a Zeiss three-prism spectrograph. The light of a carbon arc was passed through a red filter transmitting wavelengths greater than 6300 Å and focussed on the diamond. After one minute of exposure, the diamond was activated again and the experiment repeated 30 times. A faint spectrum (not reproduced) was obtained in the violet part and showed the 4152 line and its system of bands. To prove that the spectrum was not due to fluorescence, a blank experiment was performed in which the diamond was not activated with the mercury arc but a continuous exposure of one hour and a half was given with red light focussed on the diamond as before. In the spectrum, no trace of the violet portion was found and only the band in the red region due to the incident light appeared.

In the case of the brightly green-fluorescent diamond N.C. 41, the 5032 line and its bands were found faintly with an exposure repeated 50 times in the manner described above.

4. The Effect of Heat

It has been stated that the diamonds retain energy for several days after activation. The activated blue-fluorescent diamonds on heating to 270° C. exhibit blue thermoluminescence as stated in the paper on thermoluminescence. After a few minutes the glow disappears, and after cooling the diamond shows no longer any flash on irradiating with red light and observing through copper sulphate solution. In the case of the green-fluorescent diamond N.C. 41, a faint greenish yellow thermoluminescence is observed on heating to 270° C. and subsequently the usual flash with red light is absent. Thus at 270° C. the diamonds lose their activation.

On cooling the diamonds by immersing in liquid air, they showed every one of the usual effects resulting from activation.

In conclusion, the author wishes to express his deep gratitude to Professor Sir C. V. Raman for his inspiring guidance and for his helpful interest in the problem.

5. Summary

Fluorescent diamonds retain some energy after ultraviolet irradiation, a part of which is released at room temperature as phosphorescence. However, a greater part of the energy remains with the diamond for any length of time until it is illuminated with long wavelength radiations; it is then emitted as a flash of visible light. This can be observed through a proper filter complementary to the illuminating light. Any wavelength above 4200 Å is able to remove the activation in diamonds. Ultraviolet light below 3000 Å produces activation several times greater than that produced by the very near ultraviolet between 3500 and 4100 Å. X-rays are also capable of producing a weak activation. All these effects are observed even at liquid air temperature. However, the activation in diamond can be removed by heating it to 270° C. when thermoluminescence is observed. In the case of blue-fluorescent diamonds, the stored-up energy is given out mainly as a blue flash on illuminating them with long wavelength radiations and the spectrum of the flash reveals mainly the 4152 system, while in green-fluorescent diamonds, green light is mainly emitted and the 5032 system is found in the spectrum of the flash.

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